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## USSR REPORT

## CHEMISTRY

No. 95

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## ADSORPTION

UDC 541.183

ADSORPTION THEORY AND ITS APPLICATION TO CHROMATOGRAPHY OF OLIGOMERS ON BASIS OF MOLECULAR MASS AND FUNCTIONAL GROUPS: APPLICATION TO LINEAR OLIGODIENES AND OLIGOESTERS AND -ETHERS WITH TERMINAL FUNCTIONAL GROUPS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 11, Nov 82  
(manuscript received 3 Aug 81) pp 2641-2655

GORSHKOV, A. V., FILATOVA, N. N., ROSSINA, D. Ya., YEVREINOV, V. V. and ENTELIS, S. G., Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] A presentation is made of the mathematics involved in delineating the optimum parameters for the chromatographic resolution of reactive oligomers, with particular attention to the separation of hydroxy and carboxy group-containing linear oligobutadienes, polyesters, and polyethers on silicagel. The approach is based on the evaluation of the distribution coefficients and retention volumes in relation to the adsorption energies of the groups in question which were determined on the basis of Snyder's correlation parameters. Figures 7; references 16: 11 Russian, 5 Western.  
[79-12172]

UDC 511.182:541.6

ADSORPTIVE PROPERTIES OF CHEMICAL FIBERS AND POLYMERS

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 55, No 10, Oct 82  
(manuscript received 19 Apr 82) pp 2299-2303

GREBENNIKOV, S. F. and KYNIN, A. T.

[Abstract] Chemical fibers and polymers are finding increasing application in sorption technology and as construction materials. Thus it is essential to know the principles of the sorption. Previously it was shown that vapor sorption on swelled polymers can be described by an equation of the volume micropore filling theory. This equation is presented and discussed. Since sorption properties depend on thermodynamic affinity of sorbate and sorbent, and every group of polymers must be characterized more precisely, the authors developed more precise measurement procedures. Where vapor does not cause swelling, ordinary physical adsorption occurs. Micro-, and meso- and macropore are progressively more-pronounced faults that decrease durability, so the latter

categories are not typical for production-chemical fibers. Study of porous structures and sorption of inert and active vapors on capron, lavsan, nitron and other fibers, and specialized fibers based on polyacrylonitrile, polyvinyl alcohol and cellulose hydrate showed they could be classified as sorbates using the equation for the theory of volume micropore filling. Figure 1; references 10 (Russian).  
[55-12131]

## ALKALOIDS

UDC 547.462.3(008.8)

### SYNTHESIS OF N-SUBSTITUTED ALKALOID METHACRYLAMIDES

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 4, Jul-Aug 82  
(manuscript received 17 Nov 81) pp 30-33

KHVAN, R. M., BABAYEV, T. M. and MUSAYEV, U. N., Tashkent Order of Labor Red Banner State University imeni V. I. Lenin; Institute of Bioorganic Chemistry, UzSSR Academy of Sciences

[Abstract] Synthesis of monomers based on physiologically active compounds is of pharmacological interest. The authors used N-substituted acryl- and methacrylamides derivatives of anabazine and piperidine, in reinforced laboratory tests to produce greater yields and develop production procedures. They determined that monomer yield depended on reagent ratios, duration of their contact and temperature of the reaction. The monomers formed at room temperature, but increasing the temperature to the mixture's boiling point of 95-97° C shortened reaction time markedly. Chemical structures were confirmed by microanalysis, chromatography, and infrared, PMR and mass-spectroscopy. The N-methacryloylanabazine and N-methacryloylpiperidine produced were used to synthesize physically active, water-soluble polymers. Chemical procedures are given. Figures 4; references 3: 2 Russian, 1 Western.  
[38-12131]

## LIQUID CHROMATOGRAPHY OF ALKALOIDS, PART 4: MOLECULAR ADSORPTION OF ALKALOIDS ON HYDROPHILIC AND HYDROPHOBIC GELS

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5, Sep-Oct 82 (manuscript received 22 Apr 82) pp 37-43

GLADYSHEV, P. P. and MATANTSEVA, Ye. F., Order of Labor Red Banner Institute of Chemical Sciences, KaSSR Academy of Sciences, Alma-Ata

[Abstract] Various organic gel sorbents are presently used to identify and analyze natural compounds. An example is sephadex, which when synthesized from polydextrans is a hydrophilic gel, but which is alkylized to obtain more hydrophobic properties. The authors studied balanced distribution of alkaloids among various types of sephadexes and the external solution with zero adsorbent filling using analytical chromatography. Quasihomogeneous and heterogeneous sorbents and their characteristics are discussed: the latter type was used in this experiment. The portion of a sorbent's volume available to a sorbate depends on its molecular mass, a phenomenon called the molecular screen effect. For sephadexes there is no conformation of the hypothesis that matrix fragments are found as ligands. Theoretical and experimental data indicate that in a broad range of concentrations, sorption does not depend only on content of the basic electrolyte in the external solution, but on the pH factor as well. The neutral form of alkaloids adsorbs more strongly than the ionized one. Hyperproportional increases in sorption with increasing density is related to the appearance in dense gels of bands corresponding to alpha-, beta- and gamma-cyclodextrins. Figures 5, references 13: 7 Russian, 6 Western. [37-12131]

LIQUID CHROMATOGRAPHY OF ALKALOIDS, PART 5: REVERSE PHASE CHROMATOGRAPHY OF OPIUM ALKALOIDS ON Bondapak C<sub>18</sub>/Corasil

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5, Sep-Oct 82 (manuscript received 22 Apr 82) pp 44-50

GLADYSHEV, P. P. and MATANTSEVA, Ye. F., Order of Labor Red Banner Institute of Chemical Sciences, KaSSR Academy of Sciences, Alma-Ata

[Abstract] Silicate adsorbents with grafted hydrophobic phases are frequently used for rapid chromatographic separation of many natural compounds, including the title variant. The authors tested the process against standards for morphine, codeine, narcotine, thebaine and papaverine. Calculations, based on minimizing square deviations between theoretical and experimental values with FORTRAN, determined reaction constants, leading to the hypothesis that these deviations were caused by ionization of silanol groups that remained after hydrophobization of the silica surface. The complex sulfaphobic theory is explained. The

temperature dependence of distribution coefficients in reverse phase processes is determined by enthalpy of sorbate-ligand association when the temperature range does not lead to changes in the structure of the stationary phase and the sorbate. At the optimum temperature of 60°C, the process permitted separation of the five basic opium alkaloids in 35 minutes. Figures 4, references 15: 7 Russian, 8 Western.  
[37-12131]

UDC 541.49:543.253

VOLTAMMETRIC STUDIES OF PALLADIUM-ORGANOPHOSPHORUS LIGAND COMPLEXES IN DIMETHYLFORMAMIDE

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 27, No 11, Nov 82  
(manuscript received 25 Mar 82) pp 2983-2984

GAZIZOV, K. K., YUKHNOVICH, D. M., BUDNIKOV, G. K., POLOVNYAK, V. K. and AKHMETOV, N. S., Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] The electrochemical behavior of palladium complexes with organophosphorus ligands of the  $PdL_2X_2$  type, where  $L = PPh_3$  or  $P(OPh)$  and  $X = Cl^-$  or  $CNS^-$ , were investigated on a platinum microelectrode in dimethylformamide. Calculation of Semerano coefficients for the reduction and oxidation peaks pointed to diffuse electrochemical processes that were irreversible. In addition, replacement of  $Cl^-$  by  $CNS^-$  resulted in a cathode overload while replacement of  $PPh_3$  by  $P(OPh)_3$  retarded electro-reduction of the palladium (IV) complex on the electrode, but facilitated reduction of the palladium (II) complex to the palladium (0) complex. Figures 1; references 2 (Russian). [80-12172]

UDC 547.466'468:539.1.04

$^{31}P$  and  $^1H$  NMR STUDIES ON POLYCRYSTALLINE NITRILOTRIMETHYLPHOSPHONIC ACIDS

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 27, No 11, Nov 82  
(manuscript received 30 Dec 81) pp 2756-2758

POPOV, K. I., LARCHENKO, V. Ye., CHUVAYEV, V. F. and DYATLOVA, N. M., Moscow Food Industry Technological Institute; Moscow Aviation Institute imeni S. Ordzhonikidze

[Abstract]  $^{31}P$  and  $^1H$  NMR studies were conducted on polycrystalline nitrilotrimethylphosphonic acid (I) and its barium and strontium salts at 20 and  $-196^\circ C$ , which demonstrated that five of the six 'acid' protons possess translational motion and that the  $PO_3^{2-}$  groups rotate around the P-C bond in the acids but not in the salts. Analysis of the values of the secondary moments and the intensities and forms of the NMR line confirmed X-ray structural data on the betaine structure of I. Figures 1; references 4: 2 Russian, 2 Western. [80-12172]

## ATOM ABSORPTION METHODS OF ANALYZING COMPLEX ALLOYS USED IN ELECTRONICS

Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA  
KHIMICHESKIKH NAUK in Russian No 12, Issue 5, Sep 82 (manuscript received  
14 Oct 81) pp 73-76

PAPINA, T. S., YUKSHINSKAYA, L. A. and YUDELEVICH, I. G., Institute of Inorganic  
Chemistry, Siberian Division, USSR Academy of Sciences, Novosibirsk

[Abstract] A prerequisite in producing dependable semiconductor instruments is maintenance of precise technological procedures. To meet the demands of chemical parameters for electrode alloys the authors developed the title methods to analyse alloys based on Pb and In with alloying additives of Sn, Bi, Ga, Au, Sb and Ni. While some such alloys have previously been analyzed, it was essential to study the effects of a base on the atom-absorption assay of each component of such alloys and of their joint effects in solutions. Chemical procedures are summarized in the experimental section. It was necessary to maintain a definite acidity with respect to HCl in the comparison and test solutions because HCl influences the magnitude of the analytical signals of Ga and In, and because salts of Sn, Bi and Sb hydrolyse in weak acid solutions. Results showed that only lead had a major effect on the analytical signal of tin and antimony; all others could be ignored. In dissolving the alloy PbInBiSbGaAu it was unnecessary to transfer all lead into solution since no coprecipitation of other components of the alloy onto PbCl<sub>2</sub> took place. Excessive loss of tin and antimony was prevented by dissolving them in glass containers and distilling them under an infrared lamp. Standard samples were compared to confirm test results. Figures 3; references 10: 8 Russian 2 Western.  
[57-12313]

UDC 541.49:546.98

## REACTION OF PLATINUM METALS WITH TRIPHENYLTHIOPHOSPHITE

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 55, No 10, Pct 82  
(manuscript received 30 Dec 80) pp 2303-2306

SIMANOVA, S. A., KRYLOVA, G. S. and KUKUSHKIN, Yu. N., Leningrad Technological  
Institute imeni Lensovet

[Abstract] Gravimetric methods for assaying platinum metals are of interest in controlling extraction and concentration processes. The authors studied the conditions for precipitating platinum metals with TPTP from neutral and acid solutions, as well as the phosphite's reaction with Fe<sup>3+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup>. Isolation of rhodium, palladium, ruthenium, osmium, iridium and platinum is described, and the most successful extraction methods summarized.



With a chloride complex, the platinum metals were practically completely separated. Among base metals, only copper was precipitated by TPTP. The mechanism of the process was determined using the examples of chloride complexes of palladium and rhodium. The precipitation involved formation of compounds such as  $M(C_6H_5S)_2$  and  $M(C_6H_5S)_3$ . References 10: 9 Russian, 1 Western. [55-12131]

UDC 661.635+546.185

NATURE OF CONNECTION OF CERTAIN PHYSICOCHEMICAL PROPERTIES OF MELTS OF METAPHOSPHATES OF ALKALI AND ALKALINE EARTH METALS WITH NATURE OF CATIONS

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5, Sep-Oct 82 (manuscript received 25 May 82) pp 1-5

ROZHNOV, V. B., SERAZETDINOV, D. Z. and BEKTUROV, A. B., Order of Labor Red Banner Institute of Chemical Sciences, KaSSR Academy of Sciences, Alma-Ata

[Abstract] The authors studied the title relationship in connection with use of condensed phosphates as fertilizers, assaying viscosity and density. Previous measurements of viscosity had been distorted by dissolution of part of the corundum-coated vessel used in the tests. The present tests were done on a vibration viscosimeter and density by a method involving weighing the platinum body of the vessels used. Higher viscosity and activation energy were found for alkaline earth than for alkali metals. Changes in density of alkaline earth metals correlated with the growth in the atomic weight, while for alkali metals the correlation was destroyed by the anomalous behavior of  $KPO_3$ . A straight-line dependency affirms the role of cation polyhedron density in the process of viscous flow of metaphosphate melts. Steric hindrance hindered cooperative shifting of bonds. It was hypothesized that in melts with changing ratios of metal oxides and  $P_2O_5$  the activation energy was directly proportional to the coefficient of structure bonding and equal to the sum of coefficients of "density" of oxygen polyhedrons of cations and phosphorus. Figures 4; references 14: 11 Russian, 3 Western. [37-12131]

STUDIES OF SULFATOPHOSPHATES, PART 6: THERMAL CONVERSIONS OF EQUIMOLAR MIXTURES OF POTASSIUM AND MAGNESIUM SULFATES IN PRESENCE OF VARIOUS QUANTITIES OF PHOSPHORIC ACID

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5, Sep-Oct 82 (manuscript received 28 May 81) pp 6-12

BEKGUROV, A. B., LITINENKO, V. I. and ORDABAYEVA, A. A., Order of Labor Red Banner Institute of Chemical Sciences, KaSSR Academy of Sciences, Alma-Ata

[Abstract] Continuing study of previously obtained solutions of concentrated PKMg products for fertilizers, the authors studied reaction of mixed potassium and magnesium phosphates at 400-900°C with various amounts of phosphoric acid, durations and cooling periods. The initial mixtures were placed in platinum jars and held at a steady temperature for 1 hour, then cooled rapidly. Results showed that with increased temperatures up to 700°C, there was loss of weight, general content of  $P_2O_5$ ,  $K_2O$  and  $MgO$  and a drop in sulfur content. Less noticeable losses came at 700-900°C. Products obtained at 400-500°C did not dissolve completely in HCl. With increased amounts of phosphoric acid up to 3-4 moles,  $SO_3$  losses increased. Solubility in water and a 2% citric acid solution was increased by raising the amount of phosphoric acid. Chemical analysis data indicated that the amount of potassium oxide remained constant throughout the temperature range and was unchanged from the initial amount.  $MgO$  and  $P_2O_5$  amounts were distributed between soluble and insoluble forms up to 700°C, while above that temperature they went into solution with the 2% citric acid, almost completely. The results showed procedures for producing the desired fertilizer from phosphorite, polyhalite and sulfuric acid. Figures 4; references 13: 9 Russian, 4 Western.

[37-12131]

UDC 548.736

SYNTHESIS AND PHYSICOCHEMICAL STUDY OF NEW URANYL HYDROXOSULFATES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 266, No 5, Oct 82 (manuscript received 28 Apr 82) pp 1148-1152

KOVBA, L. M., TABACHENKO, N. V. and SEREZHKIN, V. N., Moscow State University imeni M. V. Lomonosov; Kuybyshev State University

[Abstract] The title hydroxosulfates are among the most interesting secondary uranium minerals because of their structure and properties. The authors investigated crystals of johannite and the possibility of obtaining cuprozippeite as well as of synthesizing and studying physicochemical properties of their analogs. The hydrothermal synthesis of these compounds was followed by thermogravimetric, X-ray phase, X-ray structure and high temperature X-ray

photographical analysis methods. The thermal decomposition of johannite was accompanied by a three-stage dehydration. Thermal decomposition of hydroxosulfatouranilate of zinc showed that at 180°C this compound lost 1.5 molecules of water and formed an intermediate compound  $\text{Zn}(\text{UO}_2)_2\text{SO}_4(\text{OH})_4$ . X-ray photography showed a similarity of data for compounds with natural and synthetic zippeites. The authors' results differed from previous related studies. Figures 2; references 10: 5 Russian, 5 Western.  
[60-12131]

## CATALYSIS

UDC 541.128

### THEORY OF POLYHEDRON TYPE CATALYSIS AS BASIS FOR SYNTHESIS OF INDUSTRIAL CATALYSTS, PART 4: CONTROL OF CATALYST COMPOSITION AND STRUCTURE

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 11, Nov 82  
(manuscript received 11 Nov 80) pp 2727-2729

KOLESNIKOV, I. M., BAYANOVA, N. N. and TETERIN, Yu. A., Moscow Institute of Petroleum Chemical and Gas Industry imeni I. M. Gubkin

[Abstract] X-ray photoelectronic and fluorescence spectroscopies were used to analyze the catalytic properties of solid catalysts in relation to their structure and composition. The resultant findings confirmed previously reported data on the relationship between catalytic activity and the composition and structure of the polyhedrons within the polyhedral complexes of zeolites. Figures 3; references 9: 6 Russian, 3 Western.  
[79-12172]

UDC 541.128.1+541.128.38

### CATALYTIC ACTIVITIES OF MONOMERIC AND DIMERIC $\text{Fe}^{3+}$ EDTA COMPLEXES AND MAGNETIC FIELD EFFECTS ON RATE OF HYDROGEN PEROXIDE DECOMPOSITION

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 11, Nov 82  
(manuscript received 25 Oct 81) pp 2740-2743

AFONIN, V. V., VANAG, V. K. and KUZNETSOV, A. N., Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] Investigations were conducted on the catalytic decomposition of hydrogen peroxide by  $\text{Fe}^{3+}$  EDTA complexes with the concentrations of  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  adjusted to favor catalysis either by  $\text{Fe}^{3+}$  EDTA monomeric or dimeric complexes at 22°C, pH 9.1,  $I = 0.45$ . Investigations on the effects of an induced magnetic field showed that, contrary to other reports, exposure to magnetic field had no effect on the catalysis by either the monomeric or dimeric complexes. Figures 2; references 7: 6 Russian, 1 Western.  
[79-12172]

## GENERATION OF Pt-Pd CATALYSTS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 11, Nov 82  
(manuscript received 24 Jul 81) pp 2852-2854

SOKOL'SKIY, D. V. and CHATYBEKOVA, Sh. Ye., Institute of Organic Catalysis  
and Electrochemistry, Kazakh SSR Academy of Sciences, Alma-Ata

[Abstract] Investigations were conducted on the relative ratios of Pt and Pd in Pt-Pd catalysts synthesized in a 1:1 ratio and employed for the hydrogenation of dimethylethynyl carbinol. The results of physico-chemical analysis of the catalyst surface (electron microscopy), X-ray spectral fluorescence and photo-electronic spectroscopy) showed that, with time, the content of Pd on the surface (5-10  $\mu\text{m}$ ) became 1.5-2-fold greater than that of Pt, confirming earlier findings by others that relied on potentiometric and kinetic methods. Figures 5; references 2: 1 Russian, 1 Western.  
[79-12172]

UDC 66.028/088.8

## APPARATUS FOR CONDUCTING CATALYTIC REACTIONS

Kiev KHIMICHESKAYA TEKHNLOGIYA in Russian No 5, Sep-Oct 82 (manuscript received 20 Aug 81) pp 27-28

POLYAK, M. L., Odessa Petroleum Processing Plant

[Abstract] Sulfuric acid production involves catalysis of gases containing 7-11%  $\text{SO}_2$ , in which exothermal catalysis releases significant amounts of heat and the equipment temperature reaches 450° C. The author developed an apparatus to accomplish this necessary heating when concentrations of gas are too low for such heat production. The apparatus (illustrated) brings even heating of the contact mass throughout the chamber, with the heat produced in catalysis being used to heat incoming gases before they are oxidized. Figure 1; references 2 (footnotes in Russian).  
[33-12131]

CONVERSION OF ALCOHOLS INTO CARBONYL COMPOUNDS ON D-53 CATALYST

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 10, Oct 82 pp 583-585

AZIZOV, M. M., KARIMOV, P. Kh., ABDURAKHMANOV, M. A., KADYROVA, T. D. and SIDIKOVA, M. N.

[Abstract] Earlier research tested a highly-effective catalyst--involving oxidation-dehydrogenation of methanol to formaldehyde--in place of the usual silver on pumice, and named it D-53. The authors sought to use it to synthesize methylethylketone from secondary butanol to use it--instead of silver on aluminum oxide--in obtaining acetone from wastes of technical isopropanol production. The oxidate was analyzed for methylethylketone, starting alcohol, acetone, acetaldehyde and water, in the first instance, and for acetone, alcohol and water in the second. Data indicate that as the volume delivery rate of azeotrope was increased from 10 to 28<sup>-1</sup> parts, yield of methylethylketone as a percentage of the starting alcohol declined on both catalysts, while ketone yield increased. The process parameters were consistently higher for the D-53 catalyst than for the pumice-silver catalyst, or for the silver-aluminum oxide catalyst in acetone production from isopropanol wastes.

[58-12131]

## CHEMICAL INDUSTRY

### CHARDZHOU CHEMICAL PLANT ADDS AFRICA TO EXPORT LIST

Ashkhabad TURKMENSKAYA ISKRA in Russian 15 Sep 82 p 4

[Article by B. Dzhumayev: "In 40 Countries of the World"]

[Text] Up until now, products bearing the brand of the Chardzhou Chemical Plant imeni V. I. Lenin were known only on the Asian and American continents. Now countries of the African continent have appeared on the list of its exporters. The first large consignment of storage battery acid was shipped to Angola, Libya and Mali.

This is no longer the first year that the plant's products are being shipped to Cuba, Mongolia, Iraq and other countries. Some of these countries get aluminum sulfate produced on the basis of the most sophisticated technology from Chardzhou. It is not inferior in quality to the best in the world, which is why the demand for it is growing with every year.

11004

CSO: 1841/62

## COMBUSTION

UDC 536.46

### TWO-DIMENSIONAL INSTABILITY OF COMBUSTION FRONT WITH PARALLEL REACTIONS

Moscow KHIMICHESKAYA FIZIKA in Russian No 10, Oct 82 (manuscript received 25 Mar 82) pp 1412-1420

ALDUSHIN, A. P. and KASPARYAN, S. G., Department of Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka

[Abstract] Various studies have examined stationary combustion in which two parallel reactions are occurring and different results take place simultaneously. The authors have analyzed stability of a stationary wave where one- and two-dimensional disturbances are found throughout the area of stationary regimes. Thermal physics factors are seen as independent of temperature and mixture composition. The kinetics of each reaction are assumed to have a zero order with respect to concentration and a sufficiently high energy of activation. Linear analysis is made of the dispersion ratio and parameters for wave stability of combustion in the parallel reactions calculated. These parameters characterize the sensitivity of stationary rate and combustion temperature to changes in the mixture temperature. A parallel is noted between combustion zone expansion and competing reactions and heat patterns of heterogeneous exothermal reaction. Also calculated are stability of the front of parallel reactions with Lewis numbers  $L \leq 1$  and stability of non-diffusion combustion, where a boundary of monotonic instability of the flat front in parallel reactions was noted. Back combustion waves are regarded to indicate preservation of an unstable intermediate pattern. Figures 5; references 15 (Russian).  
[39-12131]

UDC 536.46

### COMBUSTION OF N POWDER IN TURBULENT FLOW

Moscow KHIMICHESKAYA FIZIKA in Russian No 10, Oct 82 (manuscript received 16 Apr 82) pp 1421-1427

BELYAYEV, A. A., ZENIN, A. A., KULESHOV, V. V., LEYPUNSKIY, O. I., NOVOZHILOV, B. V., and POSVYANSKIY, V. S., Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] The phenomenon an increase in rate of combustion of a powder, under blowing upon its burning surface with a stream of combustion products was



discovered by Leypunskiy in 1942; under the name of erosion burning it has received much attention, but such questions as the existence of a speed "threshold" and negative erosion remain open, and no comprehensive theory has been developed. The authors made experimental studies with a microthermocouple method that permitted determination of local burning rate as well as temperature distribution by combustion zones. They developed a theory based on calculating the combustion rate and temperature distribution during blowing based on macrokinetics of chemical reactions conducted without blowing. The design of the apparatus and the microthermocouple methodology are summarized in the experimental section. The theory behind the calculations, and previous research that confirms their findings, are outlined. The tests provided temperature zone profiles, pressure variation intervals, surface temperatures and heat dispersion from gas into the condensed phase. A satisfactory correlation between theoretical and experimental values was obtained. Figures 4; references 16 (Russian).  
[39-12131]

UDC 614.841.41:547.593

PREDICTING CONCENTRATION FLAMING LIMITS OF VAPORS OF CERTAIN ALIPHATIC ALCOHOLS AND COMPLEX ETHERS IN AIR AND FLAME POINTS WHEN AIR IS DILUTED WITH NITROGEN OR CO<sub>2</sub>

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 7, Jul 82  
(manuscript received 5 Aug 81) pp 860-865

KHRAMOV, V. V., SHUSTROV, N. I. and BOBKOV, A. S., Branch of All-Union Scientific Research Chemico-Pharmaceutical Institute imeni S. Ordzhonikidze, Moscow Oblast

[Abstract] The authors sought to determine the applicability of the method of calculations developed for saturated aliphatic hydrocarbons based on the balance of tear and branching probability and thermophysical properties to predict low and high limits of concentration flame point for the title complexes. The method, involving determination of the point of kinetic balance and the critical temperature, is applied to methanol, ethanol, n-propanol and n-butanol, and calculations are given. It is noted that the calculation error increases as the method moves from hydrocarbons to alcohols, but does not exceed 15%. The method is given step by step. A satisfactory correlation was found between theoretical and experimental data. References 10: 7 Russian, 3 Western.  
[41-12131]

## THEORY OF LIMITS OF COMBUSTION FLAME SPREAD ON SURFACE OF BURNING MATERIALS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 266, No 4, Oct 82  
(manuscript received 19 May 82) pp 915-918

RYBANIN, S. S., Chernogolovka Department, Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka, Moscow Oblast

[Abstract] The question of combustion limits and flame spread in an oxidizing medium has taken on great importance with the increased use of synthetic materials in industry, transportation and home consumption. The author considers flame spread on materials where heat emission occurs in the gaseous phase as a result of chemical reactions between oxidants of the environment and products of the gasification of the material. Research has shown that the intensive chemical reaction begins only at some distance from the surface of the burning material. Calculations are presented to determine the location of this "burning edge" or rim where gas being formed and oxidants from the surrounding environment meet. The author concludes that flame spread cannot occur on the surface of the material if the thickness of the surface layer is greater than the lower limit of inflammability. Natural convection and oxidant concentration also affect flame spread. A further factor influencing oxidant concentration and thus combustion is gas pressure. A drop leads to heat losses and an increase in the concentration limit of the oxidant. Figure 1; references 10: 8 Russian, 2 Western.  
[27-12131]

UDC 614.844:66

## NEW FIREFIGHTING MEANS IN CHEMICAL INDUSTRY

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 10, Oct 82 pp 607-612

BARATOV, A. N. and MYSHAK, Yu. A.

[Abstract] Increased effectiveness and review of current methods for extinguishing chemical fires offer potential improvements in fire safety. The present article deals with new advances in developing homogeneous and heterogeneous fire inhibitors. The former are coolants such as bromofluorohydrocarbons, while heterogeneous inhibitors include, chiefly, powders based on alkaline earth metals. The mechanism of such chemicals in fire extinguishing is explained as a point of departure. While powders have advantages in cost, availability and effectiveness, they are not coolants and thus flame can reignite. Also, they tend to pack and do not transport well. Research has endeavored to improve both chemical and mechanical properties of powders, partially by pinpointing their inhibiting ability as heterogeneous recombination of active centers on the surface of solid particles. These studies have led to new powder compositions that improve viscosity and resist packing. Other

efforts have been in the direction of combining the advantages of coolants and powders, as for substances for extinguishing benzine fires. Difficulties in using gas-liquid or gas-powder extinguishing agents include preparation and maintenance. Reports of previous research and experimental data gathered by the authors were used to select a gas-liquid ejector, whose design is diagrammed and described. Further study is needed of specific extinguishing substances for particular types of chemical fires. Figures 3; references 22: 21 Russian, 1 Western.

[58-12131]

## FERTILIZERS

### KEMEROVO 'AZOT' PRODUCTION ASSOCIATION FAILS PLAN

Moscow EKONOMICHESKAYA GAZETA in Russian No 39, Sep 82 p 19

[Article by V. Ovcharov: "Chemists Fall Back"]

[Text] The Kemerovo "Azot" Production Association, one of the largest suppliers of mineral fertilizers to Siberian agricultural regions, recently experienced a dramatic worsening of its work. In 8 months the enterprise produced 30,000 tons less fertilizers than foreseen by the plan (corrected for 100-percent nutrient concentration). It was also short by over 60,000 tons of ammonia, the principal raw material used in nitrogen fertilizer production. Also behind is production of caprolactam and methanol, the principal ingredients used in production of synthetic fibers, cord and plastics.

When socialist pledges were adopted at the beginning of the year in the Kemerovo "Azot" (association director V. G. Koptelov and chief engineer A. P. Pronin), the promise was made that the plan would be exceeded by 2,600 tons of mineral fertilizers, 1,400 tons of ammonium and other products, and that all quality indicators would be improved. Unfortunately the pledges never materialized.

In the recent past, meanwhile, the association was a progressive, stably operating enterprise, serving as an example to other collectives.

In May-June the equipment in the main production shops underwent planned overhaul. An improvement in machine unit operation would have been expected. In fact, however, the opposite happened--serious problems began to occur in July, leading to failure of the production rhythm.

Concern for building new facilities and placing new productive capacities into operation weakened in the association. Recently a unique high-output carbamide production unit was put into operation late here. It is taking a long time to raise its indicators to the planned level.

Simultaneously with eliminating the shortcomings in the operating shops and reinforcing production discipline, we must improve organization of capital construction. After all, before the end of the 11th Five-Year Plan large capacities producing fertilizers and raw materials for them are to be placed into operation at the enterprise.

The association collective possesses great potentials for highly effective work. It has qualified personnel and chemical specialists. It has a strong material-technical base. We would hope that in the time left until the end of the year, the association will catch up.

11004

CSO: 1841/62

## FREE RADICALS

UDC 541.515+541.138.2+541.138.3

### ENERGY FEATURES OF ELECTROCHEMICAL OXIDATION-REDUCTION REACTIONS OF FREE RADICALS AND ION RADICALS

Moscow ELEKTROKHIMIYA in Russian Vol 18, No 10, Oct 82 (manuscript received 27 Jul 81) pp 1415-1417

POKHODENKO, V. D., PLATONOVA, E. P. and KOSHECHKO, V. G., Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, UkSSR Academy of Sciences, Kiev

[Abstract] Recently the authors established several principles of cathode reduction and anode oxidation of a number of stable free electron-neutral radicals, and various classes of cation- and anion-radicals. In the present study the authors compared electrochemical reduction and oxidation for free radicals and organic molecules with even numbers of electrons, using the examples of 2,6-di-tert-butyl-4R-phenoxy and substituted triphenylverdazyl free radicals, cation radicals of substituted phenazines and triphenylamines, and anion radicals of substituted para- and ortho-benzoquinones. The linear nature of the dependence of reduction and oxidation conversion of organic compounds with an even and odd number of electrons is summarized. References 17: 10 Russian, 7 Western.  
[59-12131]

UDC 541.135.27

### CROSS-ANODE COMBINATION IN PRESENCE OF ETHYLENE AS A RADICAL ACCEPTOR

Moscow ELEKTROKHIMIYA in Russian Vol 18, No 10, Pct 82 (manuscript received 27 Jan 82) p 1438

VASIL'YEV, Yu. B., GRINBERG, V. A. and KAZARINOV, V. Ye., Institute of Electrochemistry, USSR Academy of Sciences, Moscow

[Abstract] Recently reactions involving the Kolbe synthesis with various acceptors have attracted great interest, but many factors remain unknown. The authors established for the first time that mutual electrolysis of an equimolar mixture of propionic and acetic acid in methanol on a platinum anode in the

presence of ethylene at 6 MPa pressure leads to formation of both symmetrical and "crossed" dimers of Kolbe-ethane, butane and propane through recombination. Methyl esters of both acids were also found, and the same results were obtained without adding ethylene. It is hypothesized that in this synthesis ethyl radicals were more active than methyl radicals. References 2: 1 Russian, 1 Western.  
[59-12113]

UDC 541.124

#### IMPORTANCE OF PO RADICALS IN PHOSPHORUS OXIDATION REACTIONS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 267, No 1, Nov 82  
(manuscript received 5 Jun 82) pp 110-113

ALEKSANDROV, Ye. N., ARUTYUNOV, V. S., DUBROVINA, I. V. and KOZLOV, S. N.,  
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] Kinetic and resonance-fluorescence studies were conducted on the oxidation of phosphorus to delineate the role of the PO radical in this process. The results indicated that PO radicals are formed by the reaction of  $P_4$  with O ( $P_4 + O = PO + P_3$ ) and, furthermore, that the PO radicals interact with  $P_4$  ( $PO + P_4 = P_2O + P_3$ ). Figures 2; references 15: 10 Russian, 5 Western.  
[63-12172]

## NITROGEN COMPOUNDS

UDC 547.491.307

### SYNTHESIS OF N-BUTYLISOCYANATE

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 4, Jul-Aug 82  
(manuscript received 9 Mar 81) pp 27-29

KUZIBAYEV, M. M., ATAKUZIYEV, A. A. and KADYROV, Ch. Sh., Order of Labor Red Banner Institute of Plant Substance Chemistry, UzSSR Academy of Sciences

[Abstract] Of two processes for producing the title compound (BIC), the first involves deficit butylamine and toxic, corrosive phosgene; the second, based on the reaction of butylhalide and potassium hydroxycyanide in dimethylformamide, was used by the authors to determine optimum conditions regarding ratio of reagents, temperature, and water presence. Results showed that best yields were obtained in the total absence of moisture. The authors established the proportions of 1.1 : 1 : 2.5 for BuBr, KNCO and DMF, respectively, a temperature range of 98-105°C and time of 90 minutes to obtain 90% of the theoretical yield. Chemical procedures are given. They also produced n-N,N'-dibutylurea, with 70% of theoretical yield. References 6: 3 Russian, 3 Western.  
[38-12131]

UDC 547.828

### CONFORMATION STATES OF NITROSOAMINES OF HYDROGENATED QUINOLINES AND BASES OF ALICYCLIC SERIES

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 4, Jul-Aug 82  
(manuscript received 27 Jan 81) pp 34-37

KARIMOV, M., YUNUSOV, T. K., LEONT'YEV, V. B. and NAKIBOVA, A., Tashkent Order of Labor Red Banner State University imeni V. I. Lenin

[Abstract] The physiological activity of heterocyclic nitrosoamines depends on features of spatial structure and conformation state. Substituents that change the electron characteristics alter these features. Using PMR, the authors studied tetrahydroquinoline, 2-methyltetrahydroquinoline, decahydroquinoline, ephedrine and pseudoephedrine in nitrosation reaction. Results



showed that the presence of 3 trigonal atoms in the saturated ring brought a rapidly converting "semi-saddle-1" as the form. Introducing S-substituents into six-membered systems usually changed relative isomer concentrations. Thus steric characteristics clearly changed when the valency of heteroatoms was altered. Figures 2; references 3: 1 Russian 2 Western.  
[38-12131]

## ORGANOMETALLIC COMPOUNDS

UDC 547.258.11+547.259.8

### ALLYL DEMETALLIZATION OF TIN-ORGANIC COMPOUNDS IN PRESENCE OF TETRAKIS-(TRIPHENYLPHOSPHINE)PALLADIUM (0)

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 266, No 4, Oct 82  
(manuscript received 4 Jun 82) pp 862-866

BUMAGIN, N. A., KASATKIN, A. N. and BELETSKAYA, I. P., corresponding member, USSR Academy of Sciences, Moscow State University imeni M. V. Lomonosov; Scientific Research Physical Chemistry Institute imeni L. Ya. Karpov, Moscow

[Abstract] Since cation complexes of palladium form easily as a result of oxidizing attachment of allyl halides and allyl acetates to Pd(0) complexes, these compounds could be combined with various nucleophile reagents. The authors showed that tin-organic compounds could be combined with allyl acetate in reactions that extended to various aryl-, vinyl- and allyl derivatives of tin with 5% by molecular weight of the title catalyst in hexamethylphosphorotriamide. Variations in yield are summarized; lesser yields than with allyl-, vinyl- and arylstannanes are attributed to partial decomposition of those tin-organic compounds in the amide. In less polar tetrahydrofuran the reaction took place at higher temperature. Generally, reactions of tin-organic compounds with allylacetate catalyzed by  $\text{Pd}(\text{PPh}_3)_4$  took place under mild condition with high yields and can serve as convenient methods for introducing an allyl group into organic compounds. Chemical procedures are summarized in the experimental section. References 10: 1 Russian, 9 Western.  
[27-12131]

## OCTAHEDRAL DIFLUOROPHOSPHATOFLUORIDE COMPLEXES OF PHOSPHORUS (V), ARSENIC (V) AND ANTIMONY (V)

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 266, No 4, Oct 82  
(manuscript received 22 Mar 82) pp 878-882

IL'IN, Ye. G., MAYZEL', M., SHCHERBAKOVA, M. N., VOL'F, G. U. and  
BUSLAYEV, Yu. A. corresponding member, USSR Academy of Sciences, Institute of  
General and Inorganic Chemistry imeni N.S. Kurnakov, USSR Academy of Sciences,  
Moscow

[Abstract] Phosphoryl-containing donors  $X_3PO(L)$ , with pentafluorides of niobium, tantalum, phosphorus and antimony form molecular complexes with the composition  $\vartheta F_5L$ ; the authors studied such complexes, where  $\vartheta = P, As$  or  $Sb$ , using  $^{19}F$  and  $^{31}P$  NMR. Reactions were conducted with difluorophosphoric acid that had two donor centers. Values for spectra of initial mixtures and the effects of temperature increases are discussed. Although all data were not clearly delineated, comparison of resonance signals with those for antimony pentafluoro-complexes suggested that two molecules of  $SbF_5$  attached to the  $PO_2F_2^-$ . Analogous results were recorded with arsenic complexes tested, where in comparison to  $AsF_5$  the basicity of ligands declined in the order of  $PO_2F_2^- > CH_3CN > HPO_2F_2$ . Since the reaction of  $PF_5CH_3CN$  with  $HPO_2F_2$  was accompanied by ion disproportionization and formation of  $PF_6^-$ , the actual ratio of  $HPO_2F_2 : PF_5CH_3CN$  was markedly higher than the prepared ratio. Figures 4; references 6 (Russian).  
[27-12131]

UDC 548.25:539.232

## EPITAXY FROM QUASIMOLECULAR CLUSTER OF ORGANOMETALIC COMPOUNDS AND VOLATILE INORGANIC HYDRIDES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 266, No 6, Oct 82  
(manuscript received 10 Jun 81) pp 1403-1406

DEVYATYKH, G. G. academician, DOMRACHEV, G. A., ZHUK, B. V., KAVERIN, B. S.,  
LAZAREV, A. I., KHAMYLOV, V. K. and CHURBANOV, M. F., Institute of Chemistry,  
USSR Academy of Sciences, Gorkiy

[Abstract] Production of epitaxial layers of the title compounds results in a coating whose properties depend on the purity of the initial compounds, the gas carrier and parameters of the cooling process. As the reaction involved is heterogeneous, the partial pressure of reagents is of great importance in determining the structure of the deposited layers. The authors studied various gas pressures and temperatures to determine their effects on the reaction. The apparatus permitted vacuum of as low as  $10^{-8}$  as organometallic compounds and

hydrides were introduced. Results showed that at a Knudsen number of ca. 1, the block monocrystal precipitated at above 400° C, while above 430°C coatings of GaAs developed with slight distorted lines. As temperature increased the quality of the coating improved, until above 500°C a high-quality monocrystalline coating was produced. Variations of the Knudsen number from 0.5-2 brought corresponding variations in precipitation rate, but similar quality. The luminescence of the unetched coating surface showed that it had a more intensive luminescent band than the base. The method allowed combination of the organometallic compound-hydride process with the molecular cluster epitaxial method. Figures 2; references 12: 3 Russian, 9 Western.  
[53-12131]

UDC 541.64:547.241

PROBLEMS AND SOLUTIONS IN SYNTHESIS OF OPEN-CHAIN POLYPHOSPHAZENES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 24, No 11, Nov 82  
(manuscript received 22 Mar 82) pp 2247-2267

TUR, D. R. and VINOGRADOVA, S. V., Institute of Hetero-Organic Compounds  
imeni A. N. Nesmeyanov, USSR Academy of Sciences

[Abstract] A review is provided of the problems encountered in the synthesis of open-chain polyphosphazenes, with the conclusion that polymerization of hexachlorocyclotriphosphazene (I) initially involves hydrolysis of the P-Cl bond in the presence of HCl and water, resulting in the formation of hydroxyphosphazene (II) and gaseous HCl. Subsequently, II tautomerizes into a oxophosphazane (III); the eventual protonation of the III ring by HCl and a nucleophilic attack by the nitrogen atom of the phosphazene ring leads to opening of the III ring and elongation of the polymer. Further addition of I to the active center serves as the mechanism for the growth of the polymeric chains with a terminal amino group. Polymerization of I without P-Cl bond hydrolysis, in quartz ampules in the presence of HCl, indicates protonation of the phosphazene ring and the formation of polymers with terminal amido groups that do not contain P=O bonds. These two mechanisms also suggest that, in the presence of trace quantities of water, side reactions occur among the macromolecules, in addition to elongation, which involve the terminal amino or amido group and the P-Cl bonds, which lead to formation of anomalous units within the polymeric chains. Figures 10; references 49: 19 Russian, 30 Western. [81-12172]

## THERMODYNAMIC ANALYSIS OF REACTION OF PHOSPHORUS WITH WATER

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 55, No 10, Oct 82

(manuscript received 26 Jan 82) pp 2208-2212

KIPCHAKBAYEV, A. D., YERSHOV, V. A. and MEL'NIK, A. P., Leningrad Technological Institute imeni Lensovet

[Abstract] In resolving phosphorus production problems such as high-temperature distillation of sludge, it is essential to determine the degree of the title reaction in a gaseous state as a function of temperature. It has been shown that phosphorus is oxidized by water above 1000K, while above 1300K the reaction is reversed and from 1500K the balance is shifted completely toward reduction of phosphorus oxides by hydrogen. The authors studied the nature of the phosphorus-water reaction in inert and reducing media with thermodynamic balance. Four-element P-O-H-N and five-element P-O-H-N-C systems were studied, between 600 and 4200K for the former, and 1000-4200 K for the latter. At 600-1400K basic oxidation products in the presence of nitrogen were  $P_4O_7$ ,  $P_4O_8$ ,  $P_4O_9$ , and  $P_4O_{10}$ . The contribution of uneven oxides in balanced compositions was more significant than that of corresponding  $P_4O_{10}$  and  $P_4O_6$ . In the range 1400-1800K redistribution of higher and lower oxides of phosphorus occurred, with the exception of  $P_4O_6$  and  $P_2O_3$ . Figures 4; references 8 (Russian). [55-12131]

## REACTIVITY OF ADDUCT OF TRIBUTYLPHOSPHINE WITH ETHOXYACETYLENE

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 35, No 9, Sep 82

(manuscript received 12 Mar 82) pp 583-587

MINASYAN, G. G., GASPARYAN, G. Ts., TORGOMYAN, A. M., OVAKIMYAN, M. Zh. and INDZHIKIAN, M. G., Institute of Organic Chemistry, ArSSR Academy of Sciences, Yerevan

[Abstract] Previously the authors had established that tributylphosphine reacted with alkoxyacetylene to form either phosphobetaines with a negative charge on the beta-carbon atom, or more stable monomers or dimers with a pentavalent phosphorus atom. To clarify such structures, the authors studied  $^{31}P$  spectra of the title adduct. The data obtained suggest a phosphorane structure with a pentavalent P atom in a three-membered heterocycle. In the present study, the authors considered relative reactivity of the phosphorane obtained in this reaction, comparing its electrophilicity by a competitive reaction method, to a stable phosphorus ilide and to sodium malonate. Data indicate that the title adduct is in an intermediate position as to reactivity between tributylphosphine and triphenylallylilide. Further tests with malonic

ester brought alkylation of the title adduct (84.5%) and production of an allylmalonic ester (14.5%), which is explained by the more rapid alkylation of the title adduct compared to its anionization. Chemical procedures and results of gas liquid chromatography are given in the experimental section. References 2 (Russian).

[40-12131]

UDC 547.241+547.495.1

#### ESTERS OF N,N-DIETHYLDITHIOCARBAMINIC ACID WITH CERTAIN PHOSPHORUS ACIDS

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 4, Jul-Aug 82  
(manuscript received 11 Feb 81) pp 59-61

BAKHTIYAROVA, F. A., MAKHAMATKHANOV, M. M. and MAKSUDOV, N. Kh., Tashkent Order of Labor Red Banner Institute of Engineers of Irrigation and Mechanization of Agriculture

[Abstract] Various esters of dithiocarbaminic acid have previously been described, but ones containing phosphorus have received little attention. The authors have obtained substances with phosphonyl or thiophosphonyl and thio-carbamoyl groupings, with electron-acceptor properties such that they readily react with vital enzymes of plant cells. Production of several compounds and their infrared spectra are summarized. References 2 (Russian).

[38-12131]

UDC 547.341+66.063.725

#### UNSATURATED ORGANOPHOSPHOROUS COMPOUNDS, PART 2: OBTAINING 2,6-DIPHENYL-4-(2-DIALKYL-PHOSPHORYLETHENYLIDENE)-TETRAHYDROTHIOPYRANES

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5, Sep-Oct 82 (manuscript received 10 Nov 81) pp 70-72

GODOVIKOV, N. N., KIYASHEV, D. K. and ABIYUROV, B. D., Order of Labor Red Banner Institute of Chemical Sciences, KaSSR Academy of Sciences, Alma-Ata

[Abstract] Continuing research in which they obtained acetylene organophosphoric compounds (VESTNIK AKADEMII NAUK KaSSR, 1977 No 12, pp 63-65 and 1980 No 9, pp 65-67), the authors used acetylene alcohol to produce allenes by allene-acetylene isomerization. This reaction had seldom been used to produce phosphorus-containing allenes of the thiopyrane order. The title compounds were produced in the reaction of 2,6-diphenyl-4-ethynyltetrahydrothiopyrane-4-ol with various dialkylchlorophosphites. Heating did not produce further prototropic conversion into corresponding acetylene phosphonates, but caused polymerization and formation of resin. Structures were confirmed by infrared and PMR spectroscopy. References 7 (Russian).

[37-12131]

## REACTIVITY OF PERFLUOROALKENYLFLUOROPHOSPHORANES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 267, No 1, Nov 82

(manuscript received 28 Jul 82) pp 106-109

STEPANOV, A. A. and ROZHKOVA, I. N., Institute of Hetero-Organic Compounds  
imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] Studies were conducted which demonstrated the high reactivity of perfluoroalkenylfluorophosphoranes in polar organic solvents and their use for the introduction of perfluoroalkenyl radicals into electrophilic compounds. Particular attention is accorded to the interaction of (perfluoro-2-ethylcyclobutenyl)triphenylfluorophosphorane with highly electrophilic perfluoroolefins in acetonitrile to form conjugated perfluorodienes. Reactivity of the phosphoranes in the polar solvents is ascribed to partial dissociation of the P-F bond with the formation of an ylide which attacks the perfluoroolefin to form a condensation product; in reaction with less electrophilic olefins there is also disproportionation involving the intermediate phosphonium fluoride and the starting phosphorane. References 4: 1 Russian, 3 Western.  
[63-12172]

UDC 547.241

## PHOSPHORYLATION OF ESTERS OF ACETYLSUCCINIC ACID

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 48, No 10, Oct 82

(manuscript received 14 Jul 81) pp 1063-1067

LYSENKO, V. P., GOLOBOV, Yu. G., BOLDESKUL, I. Ye. and ROZHKOVA, Z. Z.,  
Institute of Organic Chemistry, UkrSSR Academy of Sciences

[Abstract] Studies have been made previously of isolated reactions of the title acid, but none have included ethoxycarbonyl groups of trivalent phosphorus. In the present work a common method was employed for obtaining vinyl esters of phosphorus acids to conduct O-phosphorylation of the diethyl ester of acetylsuccinic acid (ethylacetylsuccinate). The structures of the compounds produced were confirmed by infrared spectroscopy. The mechanism of the reaction apparently involved initial separation of the HO-group of the enol form of the succinate with formation of the corresponding anion with a dispersed charge on the molecule. The reaction also took place successfully with dichloranhydrides of phosphorus acids. Variations include the reaction of the phosphite diethyl-[1-methyl-2,3-di(ethoxycarbonyl)-1-propenyl]-phosphite with phenylazide, which produced diethoxy-[1-methyl-2,3-di(ethoxycarbonyl)-1-propenyl]-hydroxyphosphazobenzene. This reaction required boiling in benzene, which indicated significant reduction of electron density in the phosphorus atom. PMR-spectra showed that another product, diethyl-[1-methyl-2,3-di(ethoxycarbonyl)-1-propenyl]-phosphate, was a mixture of two geometric isomers. Details of chemical procedures and spectral analyses are summarized. References 7: 3 Russian, 4 Western.  
[52-12131]



## INTRAMOLECULAR CATALYSIS IN HYDROLYSIS OF AMINOALKYLPHOSPHONIC ACID ESTERS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 82 (manuscript received 12 Jan 82) pp 2220-2223

BEL'SKIY, V. Ye., KURGUZOVA, A. M., KUDRYAVTSEVA, L. A. and IVANOV, B. Ye., Institute of Organic and Physical Chemistry imeni A. Ye. Zrbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] As bifunctional complexons, aminoalkylphosphonates contain ester bonds that can be hydrolyzed. The authors determined constants of spontaneous hydrolysis rates of diethyl esters of alpha-, beta- and gamma-substituted aminoalkylphosphonic acids. Since they have amino-groups that can undergo protonization, assay was made of the reactivity of neutral and protonized forms of the substrates. The rate constants declined slightly as the degree of protonization increased. Along with hydrolysis, breakdown occurred of the ester bond in the studied esters, apparently through intra- or inter-molecular alkylation of amino-groups. Potentiometer tests of products of hydrolysis of diethyl esters of alpha-, beta- and gamma-piperidinoalkylphosphonic acids showed no noticeable alkylation of amino-groups. References 12: 10 Russian, 2 Western.

[54-12131]

## GEMINAL SYSTEMS, REPORT 20: STRUCTURE AND PROPERTIES OF AMINOMETHYLPHOSPHONIUM SALTS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 82 (manuscript received 10 Nov 81) pp 2354-2363

KOSTYANOVSKIY, R. G., EL'NATANOV, Yu. I., SHIKHALIYEV, Sh. M., IGNATOV, S. M., CHERVIN, I. I., NASIBOV, Sh. S., ZOLOTAY, A. B., D'YACHENKO, O. A., and ATOVMYAN, L. O., Institute of Physical Chemistry, USSR Academy of Sciences, Moscow

[Abstract] The phosphonium form of the P atom is the most stable by configuration, so that PMR spectra very accurately show inequality of protons of methyl groups of the isopropyl substituent. Properties of the title salts had previously been explained by an anomalous reduction of the P atom's configurational stability, related to balance of indicator groups and the lack of supplementary signal multiplets of  $\text{CH}_2\text{N}$ . Yet in all cases equivalent spectral pictures were obtained and the chemical shifts of  $^{31}\text{P}$  of the title salts corresponded to phosphonium salts, and not phosphoranes. PMR spectra of other compounds tested also showed the equivalency of indicator groups. The most serious doubts about configurational lability of hydroxymethylphosphonium salts related to separation into antipods of chiral triarylphosphines. Factors

such as NMR parameters, phosphonium-phosphorane equilibrium, formation of a P-N bond and anomalously high quaternization, and PMR spectra, raise questions about the dependability of the results obtained. Aminomethylphosphonium salts were judged to show aminomethylating action toward nucleophiles, while phosphinomethylammonium salts did not react with them. Chemical procedures are given in the experimental section. Figures 5; references 27: 7 Russian 20 Western.  
[54-12131]

UDC 542.91:542.952.1:547.1'118

#### SYNTHESIS AND ISOMERIZATION OF O,O-DIALKYL-O-THIOGLYCIDYLTHIOPHOSPHATES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 82 (manuscript received 28 Dec 80) pp 2363-2366

NURETDINOVA, O. N. and NOVIKOVA, V. G., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Previous studies have shown that the reaction of epichlorohydrin or thioepichlorohydrin with salts of dialkylthio- or dithiophosphoric acids produces O,O-dialkyl-S-thioglycidylthiolphosphates with antifungus action. In the present study these properties were compared with those of thiol- and thionephosphates by synthesizing thionephosphates from corresponding phosphorylated derivatives of glycidene. Isomer formation hampered the study, but thione-thiol isomerization was readily monitored by  $^{31}\text{P}$  NMR. The hypothesis that isomerization could take place under the influence of either initial or subsequent ammonium or triethylammonium salts at the heating or distilling stages was tested and confirmed. Chemical procedures are summarized in the experimental section. References 4 (Russian).  
[54-12131]

UDC 542.91:541.49:547.1'128'118

#### SYNTHESIS OF BONDING BIDENTATE ORGANIC SILICOPHOSPHORIC LIGANDS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 82 (manuscript received 11 Jan 82) pp 2390-2392

BUTKOVA, O. L., ZVEZDKINA, L. I. and PRITULA, N. A., Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences, Moscow

[Abstract] Attachment of metal-complex catalysts on surfaces of inorganic oxide carriers involves bonding ligands of the title type, in which one functional group must be capable of chemical reaction with hydroxyl groups of the surface, while others form a coordinational bond with the metal-complex former. To enhance dentation the authors synthesized new compounds containing

hydrolyzing groups at the silicon atom, and electron-donor groups separated by carbon or silicocarbon fragments. Initial synthesis involved phosphines, phosphinites and phosphinophosphinites with butyl substituents at the P atom. Compositions and structures of intermediate and final compounds were determined by  $^{31}\text{P}$  NMR, infrared and mass spectra. Chemical procedures are summarized in the experimental section. References 5: 2 Russian, 3 Western.  
[54-12131]

UDC 542.97:547.1'118

#### CATALYSIS BY AMINES OF ALCOHOLYSIS OF DI-(p-NITROPHENYL)METHYLPHOSPHONATE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 82 (manuscript received 12 Jan 82) pp 2396-2399

BEL'SKIY, V. Ye., DERSTUGANOVA, K. A., BAKYEVA, R. F., KUDRYAVTSEVA, L. A. and IVANOV, B. Ye., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Kinetics of the title alcoholysis have been studied with the reaction rate varied in wide limits by changing the nature of the alcohol, the substrate and the catalyst. The catalytic activity of the amines used had only been determined for a few examples, but that information is essential for optimizing conditions of the reactions. To determine these constants the authors studied primary, secondary and tertiary aliphatic amines in the reaction of the title phosphonate with ethanol. Results showed a tertiary < secondary < primary tendency in catalytic constants; this phenomenon was related to the alkalinity of the amines. References 8: 5 Russian, 3 Western.  
[54-12131]

UDC 542.91:547.1'118

#### SYNTHESIS OF AMIDES OF THIOPHOSPHORIC ACID

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 82 (manuscript received 10 Nov 81) pp 2402-2403

KARIMOVA, P. M., TIMOFEYEV, A. I. and KNUNYANTS, I. L., Institute of Hetero-organic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

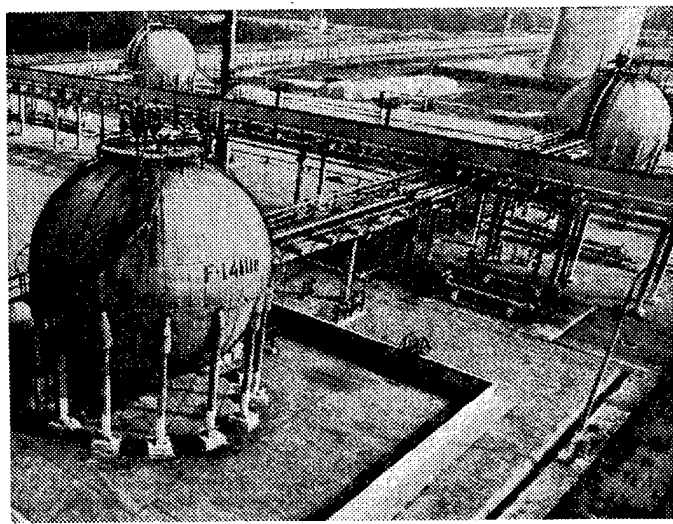
[Abstract] The fact that little has been written about the title amides stimulated the authors to synthesize several substituted amides of thiophosphoric acid as Na- and  $\text{NH}_4$ -salts through the action of alkalis on the dichloranhydride of the title amide. Compounds synthesized included previously unknown cyclohexylamido- and piperididothiophosphoric acids and piperazido-N',N''-bisthiophosphoric acid in the form of their sodium and ammonium salts. Chemical procedures are summarized. References 2 (Western).  
[54-12131]

## PETROLEUM PROCESSING TECHNOLOGY

### PETROCHEMICAL COMPLEX OPERATIONAL AHEAD OF SCHEDULE

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 11 Nov 82 p 2

[Text] Gorkiy Oblast. The planned output capacity of this petrochemical complex, which produces ethylene, propylene, ethylene oxides and glycols, was attained ahead of schedule. The complex consists of an "EP-300" unit in the city of Kstov and an ethylene oxide and glycol production operation in Dzerzhinsk. The two enterprises are joined together into a single production cycle by a 60-kilometer pipeline and three siphons crossing the river.



Portion of Complex in Dzerzhinsk

11004  
CSO: 1841/62

UDC 547.241:665.7.038.5

EFFECT OF ARYLPHOSPHITES ON ANTIWEAR PROPERTIES OF DIESEL FUELS

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 55, No 10, Oct 82  
(manuscript received 14 Nov 80) pp 2378-2380

KOVTUN, G. A. and GORBUNOV, G. V., Elektrogorskiy Branch, All-Union Scientific Research Institute for Petroleum Processing

[Abstract] Phosphorus-containing compounds have found wide application as additives to fuels and lubricants. The authors have synthesized several arylphosphite additives for diesel fuels, following standard methodology, and compared them to the standard bis(dialkyldithiophosphate)-zinc. The several arylphosphites tested are ranked with respect to their effectiveness as antiwear additives, which is proportionate to the decrease of spatial screening by ortho-substituents of the phosphorus atom. Figure 1; references 4: 3 Russian, 1 Western.  
[55-12131]

UDC 662.74:662.67

THERMAL DECOMPOSITION OF BELORUSSIAN SSR OIL SHALE

Minsk VESTSI AKADEMII NAVUK BSSR: SERYYA KHIMICHNYKH NAVUK in Russian No 5, Sep-Oct 82 (manuscript received 18 Aug 81) pp 106-109

LUK'YANOVA, Z. K., MARTINOVICH, K. B., BOLCHEK, T. M. and RUDYY, R. M., Peat Institute, BSSR Academy of Sciences

[Abstract] Recent studies of oil shale potential have turned to systematic analysis, of properties of Pripet basin deposits, particularly those of the Turovskiy area. Since use of organic material in shale is tied to its thermal decomposition, the authors assayed the widely varying content of such components as ash, carbonates, volatile gases, carbon, hydrogen and sulfur. The thermal decomposition process was found to be similar to that of Baltic kukersit shale. Since researchers have disagreed on the role of carbonates, further study was directed to clarify this parameter. Data showed that where

carbonate content in coking shale was 6.1-10.6%, pitch residue amounted to 8.2-11.4%, while with 13.0-18.0% carbonates the pitch residue was only 4.6-8.0%. The processes being used for Baltic kukersit shale were judged to be applicable to BSSR deposits. References 11: 9 Russian, 2 Western.  
[51-12131]

UDC 665.6.032.57+678.046.3

#### CHEMICAL COMPOSITION OF MINERAL PORTION OF BSSR OIL SHALE

Minsk VESTSI AKADEMII NAVUK BSSR: SERYYA KHIMICHNYKH NAVUK in Russian No 5, Sep-Oct 82 (manuscript received 19 Aug 81) pp 109-112

PROTASHCHIK, V. A. and REDINA, N. A., Peat Institute, BSSR Academy of Sciences

[Abstract] Early study of BSSR oil shales reported technical data on samples drilled at the David-Gorodokskiy site in that republic. Ash of Pripet basin shales amounts to 68.5-75.4%. Data on the chemical composition of the mineral portion of Belorussian shales has not, however, been published. The present study was done on samples from the Turovskiy deposit. Data from samples of 9 holes, taken from about 80 meters depth, contain 18.9-48.7% silicon, 10.5-36.0% calcium, 9.2-19.3% aluminum, 3.8-9.2% iron, 1.7-8.5% magnesium, 0.4-1.1% titanium, 3.9-17.0%  $SO_3$ , 0.1-0.5%  $P_2O_5$ , 0.1-0.6% sodium, 1.0-6.7% potassium and up to 11% other oxides. The results indicated sufficient variation in composition to require adjustments in processing specific oil shale deposits. References 7 (Russian).

[51-12131]

UDC 665.642.4.096+662.747.092.89

#### THERMOCONTACT CRACKING OF HEAVY PETROLEUM RESIDUES

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 10, Oct 82 pp 5-9

SOSKIND, D. M., SPEKTOR, G. S., KASATKIN, D. F. and ZENCHENKOVA, M. G., All-Union Scientific Research Institute for Petroleum Production

[Abstract] To resolve problems of processing high-tar and high-sulfur petroleum residues with boiling points of 540-600° C, the authors studied fractions with final boiling points of 500-550°C under approximated production conditions to make coking fractions. Results showed that as coking capability grew along with density and the ratio of C/H residues, yields of liquid fractions declined and coke and gas yields grew, the former markedly, the latter slightly. The only correlation of physicochemical characteristics was between product yields and coking capability of the raw material, where a linear dependence was found on the computer. Coking capability was the best measure of crude oil behavior during thermocontact cracking. The depth of asphalt removal from crude oil

in the limits studied had rather little to do with yield of low-molecular decomposition products, while yields of gas oil fractions stayed constant or increased somewhat. During thermocontact cracking the polycyclical structure of molecule nuclei was freed from the loose periphery of the tar to form gas and liquid fractions. The asphalt converted 68-84% into liquid fractions with boiling points below 500°C and gas. Combined with direct distillation of gas oil fractions, the thermocontact cracking method can be used for deep processing of nearly all crude oil. Figures 2; references 6: 5 Russian, 1 Western. [34-12131]

UDC 661.715.7:665.644

#### INCREASING PROCESSING OF AROMATIC HYDROCARBONS ON CATALYTIC REFORMING EQUIPMENT

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 10, Oct 82 pp 10-11

SKIPIN, Yu. A., YAKOVLEV, A. A. and GORODETSKAYA, G. A., "Lenneftekhim [Leningrad Petroleum Chemistry] Scientific Production Association

[Abstract] Economizing in obtaining aromatic hydrocarbons from crude oil requires improvements in raw material expenditures and reduction of the inter-regeneration cycle of equipment operation. The authors studied possible economies resulting from increasing the heat of processing to shorten time required. With other conditions held constant, temperatures were varied from 490 to 505° and results assessed on the basis of conversion of methylcyclopentane. Results indicated that even a 10° temperature increase made it possible to produce the normal year's total production in 3 months. With new polymetal, more stable catalysts of the KR series, even better results would be achieved. [34-12131]

UDC 665.767:621.3

#### WHITE OILS FOR HIGH VOLTAGE CABLES

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 10, Oct 82 pp 11-13

POTANINA, V. A., DREMOVA, T. I., MOKHOVA, L. A., PONOMAREVA, T. P., KHROMOVA, G. K. and PERMINOV, N. I., All-Union Scientific Research Institute for Petroleum Production; All-Union Scientific Research Institute for Cable Production

[Abstract] "S-220" white oil is used currently to impregnate and fill high voltage cables for 110-500 kilovolts; it has high electrical characteristics and meets production and use standards. High pressure and cooling problems, however, require filling cables with lower viscosity oils, while insulation needs still demand high viscosity. The authors developed a new white oil

similar to S-220 using a neutral oil made in producing sulfonate additives. The process involved vacuum distillation, low-temperature paraffination, sulfation with oleum, neutralizing with ammonium hydroxide and simultaneous extraction of sulfo-salts and contact purification. The lowest content of aromatic hydrocarbons was sought. Dielectric qualities varied with viscosity. Satisfactory thermooxidational capability was found at 50° C with an oil of no less than 50 mm<sup>2</sup>/sec viscosity. The final white oil had no more than 2% aromatic hydrocarbons, thus assuring high electrical insulation properties. Figure 1; references 2 (Russian).  
[34-12131]

UDC 547.298.4.621.892.86

#### THIOBENZAMIDES AS ADDITIVES TO LUBRICANTS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 10, Oct 82 pp 18-19

KULIYEV, A. B., DZHAVADOV, M. M., KULIYEV, F. A. and ABDULLAYEV, B. I.,  
Institute of Chemical Production, AzSSR Academy of Sciences

[Abstract] Earlier (NEFTEKHIMIYA 1981 pp 299-302), the authors had shown that phenyl-thioacetamides were effective lubricant additives. Continuing that work they have synthesized the title compounds by the Wilgerodt-Kindler reaction of benzaldehyde with sulfur and various amines. The structure of the compounds synthesized was confirmed by infrared and PMR spectroscopy, anti-corrosion, antiwear and antiseize properties were assayed. Up to 2% of the additive reduced corrosion from 180-200 to 14.5 g/m<sup>2</sup>; thus, the thiobenzamides were close to currently used additives and somewhat less effective than phenylthioacetamides. In antiwear and antiseize properties the thiobenzamides were close to the phenylthioacetamides, but less effective than dibenzylidene-sulfide. References 2: 1 Russian, 1 Russian translation from English.  
[34-12131]

UDC 621.892.86:621.314.212

#### EFFECTIVENESS OF ANTIOXIDANTS IN TRANSFORMER OILS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 10, Oct 82 pp 40-41

KULIYEV, R. Sh., AGAYEVA, R. A., KULIYEV, F. A. and SARKISYAN, V. M., Institute of Petrochemical Production imeni Yu. G. Mamedaliyev, AzSSR Academy of Sciences

[Abstract] Ionol, topanol-0, kerobit and other additives are used in transformer oils as antioxidants in small quantities. Numerous tests have shown that various electrophysical changes occur in Baku oils during oxidation.



Research has shown that stability can be enhanced by adding metal passivators that react to form catalytically inactive coatings. The authors studied ionol-quinizarin to determine its suitability as such an additive, and found that the combination brought significantly higher antioxidant properties and decreased consumption of ionol under conditions approaching actual use.

References 2 (Russian).

[34-12131]

UDC [66.094.34:665.521.2].002.237

#### OXIDATION OF LIGHT BENZINES TO MONOCARBOXYLIC ACIDS WITH ACETONE SEPARATION

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 10, Oct 82 pp 585-587

OGANESYAN, Sh. S. and DAYAN, V. M.

[Abstract] Acetone is one of the basic products in oxidation of  $C_3$ - $C_4$  hydrocarbons; it is produced in substantial amounts, also, in oxidation of hydrocarbon mixtures such as benzine and ligroin. The acetone yield is a function of the initial hydrocarbon content and the reaction conditions. Data show that in liquid phase oxidation of mixes of natural hydrocarbons the yield of acetone is greater than in the oxidation of individual paraffin hydrocarbons of normal structure. Other means of obtaining producing acetone also yield acetic and formic acids. When acetic acid is produced by oxidation of hydrocarbons, separation and use of the acetone byproduct is an important task consideration. The authors determined that the optimum temperature for rapid formation of  $C_1$ - $C_4$  acids and relatively low  $CO$  and  $CO_2$  yields was  $170$ - $175^\circ C$ . Recycling acetone from these processes is discussed. Oxidation of light benzines, with acetone recycling, is not regarded to be the best industrial solution. Figures 2; references 7: 4 Russian, 3 Western.

[58-12131]

UDC [661.7:547.553.2'211'126.82].004.82

#### USE OF STILL RESIDUES OF TOLUYLENE DIISOCYANATE PRODUCTION TO OBTAIN NEW BRAND OF ISOCYANATE

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 10, Oct 82 pp 589-591

SHOSHTAYEVA, M. V., GOMMEN, R. A., BOCHAROVA, V. M., TURETSKIY, L. V., SMIRNOV, S. I. and KORZHEV, A. N.

[Abstract] Environmental concerns and interest in closed cycle chemical processes have brought great attention to toluylene diisocyanate (TDI) production, which results in 16-20% tailings. In TDI distillation, phosgenization products are first concentrated by removing excess *o*-dichlorobenzene solvent, followed by periodic vacuum distilling. Various studies have dealt with

utilization of residues from the process. The authors developed a procedure for obtaining a new type of isocyanate that can be used in producing foam polyurethane (FPU) and polyurethane compounds, based on analogous reactions with polyisocyanate based on 4,4'-diphenylmethanediisocyanate. Gas-liquid chromatography indicated that the only volatile compounds in TDI production were TDI and o-dichlorobenzene. Relatively slight (30-34%) changes in NCO-group content brought significant variations in the content of TDI, high-molecular products and hydrolyzed chlorine. The high-molecular products included reactive isocyanate and carbodiimide groups as well as urethaneimine structures that tended to reverse reactions. Regardless of removal conditions, the content of NCO groups in tailings declined in direct relation to the additive ratio calculated on the basis of NCO-group content in pure TDI and in high-molecular compounds separated from tailings by n-heptane. The nature of hydrolyzed chlorine yield is also discussed. Results showed that this procedure can totally eliminate wastes at the TDI separation stage, reduce pollution and provide supplementary quantities of low-cost isocyanate for polyurethane production. Codicine production can also be combined with TDI production. Figure 1; references 10: 3 Russian, 7 Western.  
[58-12131]

UDC 615.277.3:547.586.2

DERIVATIVES OF AMINOPHENYLACETIC ACID AND THEIR ANTINEOPLASTIC ACTIVITY

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 7, Jul 82  
(manuscript received 4 Aug 81) pp 794-796

DAVTYAN, S. M., PAPAYAN, G. L., CHACHOYAN, A. A. and SAMVELYAN, K. G.,  
Institute of Fine Organic Chemistry imeni A. L. Mndzhoyan, ArSSR Academy of  
Sciences, Yerevan

[Abstract] N-acetyl derivatives of a number of amino acids have previously been described. The authors sought to expand knowledge of these compounds and find new substances with antileukemic activity by synthesizing N-phenyl derivatives of N-substituted aminophenylacetic acids as well as their methyl and ethyl esters and the methyl ester of N-phenyl-C-carbomethoxyphenylacetic acids. Then, the toxicity and antineoplastic value of these substances were studied. Toxicity was tested on white rats with several malignancies. Most of the tested substances suppressed growth of sarcomas 45 and 180 by 32-58% and generally had similar effects on other malignancies. In comparison with currently employed sarcolisin, only one compound surpassed its antineoplastic activity. Chemical procedures are summarized. References 3: 2 Russian, 1 Western.  
[41-12131]

UDC 615.33.012.6

DETERMINING DESIGN PARAMETERS OF ENZYMES

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 7, Jul 82  
(manuscript received 9 Nov 81) pp 865-868

FALKOV, N. N., SMIRNOV, R. S. and BYLINKINA, Ye. S., All-Union Scientific  
Research Institute for Antibiotics, Moscow; Moscow Institute of Chemical  
Machinebuilding

[Abstract] Wide use is being made of open turbine mixers for mixing culture liquids in biosynthetic processes. Theoretical values are summarized for the effectiveness of such mixing. The divergence between experimental and theoretical results is related to the effects of surface aeration. Its intensity and

effect on the power needed for mixing does not increase with increasing equipment capacity, as earlier calculations indicated, but rather decreases. No numerical dependency was found to determine the inter-stage distance from the intensity of liquid flow created by the operating mixing blades. The contours of circulation of upper and lower stages provided this parameter. A formula is given to express this value. Figures 2; references 4 (Russian).  
[41-12131]

UDC 615.31:547.269.3

SYNTHESIS AND BIOLOGICAL ACTIVITY OF AMINO ACID DERIVATIVES OF SULFANILIC ACID

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 7, Jul 82  
(manuscript received 5 Jan 82) pp 796-801

DIVANYAN, N. M., GALSTYAN, L. Kh., CHACHOYAN, A. A., GARIBDZHANYAN, B. T., STEPANYAN, N. O., BUNATYAN, Zh. M., PARONIKYAN, G. M., AKOPYAN, L. G., PARONIKYAN, R. V. and MNDZHOYAN, O. L., Institute of Fine Organic Chemistry, ArSSR Academy of Sciences, Yerevan

[Abstract] Continuing earlier research (this journal, 1978 No 9, pp 45-48), seeking biologically-active compounds among amino acid analogs and relationships between chemical structure and biological activity, the authors synthesized such compounds as N<sup>4</sup>-methoxycarbonylsulfanil-N-glycine, and its monoethanolamine-salt, determining their structures and compositions by infrared and mass spectra and element analysis, and their purity by thin layer chromatography. Then, hypoglycemic, antibacterial and antineoplastic effects and mutagenic activity were assayed. Hypoglycemic action, determined using *o*-toluidine reactive "Glyukoza," varied between the compounds. None had antibacterial action in tests on staphylococcus and dysentery bacilli. Their acute toxicity was very low, their antineoplastic action moderate but varied. Generally, their mutagenic action was low. References 8: 7 Russian, 1 Western.  
[41-12131]

## USING LUMINESCENT-ABSORPTION ANALYSIS AND THEORY OF IMAGE RECOGNITION TO EVALUATE BIOLOGICAL ACTIVITY OF CHEMICAL COMPOUNDS, PART 1: QUANTUM CHEMICAL INTERPRETATION OF ABSORPTION SPECTRA OF STEROID HORMONES

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 7, Jul 82  
(manuscript received 6 May 81) pp 823-826

BARENBOYM, G. M., BRIKENSHTEYN, V. Kh., OVCHINNIKOV, A. A., PITINA, L. R., TEREKHINA, A. I. and SHAMOVSKIY, I. L., Scientific Research Institute for Biological Testing of Chemical Compounds, Moscow Oblast; Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov, Moscow

[Abstract] Various parameters are used in image-recognition methods, which have become very popular in recent years. Electron spectra can be used to determine chromophores, but this data is insufficient to predict their role as a structural element and their biological activity. Using the example of steroid hormones, the authors determined minimal structural fragments of molecules and the influence of substituents in the D ring on spectral characteristics. Interpretation of ultraviolet spectra involved the Woodward rule, but its application was impossible for many classes of hormones. Quantum chemical calculations using the "PPDP" method [expansion unknown] was helpful in identifying fragments. Experimental data such as ultraviolet spectra in a vacuum confirmed theoretical values for steroid structures. A key factor was the charge on the oxygen atom, which helped determine the relationship between structure and activity. Figure 1; references 8: 3 Russian (translations ?), 5 Western.  
[41-12131]

## THERMAL PURIFICATION OF WASTES OF PRODUCTS OF SYNTHETIC MEDICATIONS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 7, Jul 82  
(manuscript received 30 Dec 81) pp 856-860

ELIK, F. I., LYAN, P. M., TIMINA, S. F. and SHUSTROV, N. I., Branch of All-Union Scientific Research Chemico-Pharmaceutical Institute imeni S. Ordzhonikidze, Moscow Oblast

[Abstract] Still residues from chemico-pharmaceutical production generally include traces of medications, resins, intermediates, organic substances and solvents, water and mineral impurities. Burning at high temperature to produce harmless  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{N}_2$  is a highly effective purification method, conducted in various types of ovens depending on the consistency and composition of residues. The authors describe the apparatus and procedures used at the Shchekin Nitrogen Production Association, where liquid residues contain compounds of sulfur and chloride. Burning should provide neutralization of

the acid gases with caustic soda. The mineral portion of the still residues consists of sodium sulfate and chloride. The composition of 10 specific residues and their chemical and physical properties are described. The chemical nature of some of these products requires caution to prevent potential explosions. Figures 2; references 4 (Russian).  
[41-12131]

## POLYMERS AND POLYMERIZATION

### MEDICAL POLYMERS INVENTED BY UKRAINIAN CHEMISTS

Kiev PRAVDA UKRAINY in Russian 2 Oct 82 p 2

[Article by Academician of the Ukrainian SSR Academy of Sciences Yu. Delimarskiy, division director, Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, and Doctor of Medical Sciences V. Zaytsev, professor, director, Kharkov Scientific Research Institute of General and Emergency Surgery: "Polymers in White Coats"]

[Text] How can we create "spare parts" and implant them into the human body? What do we do to keep such internal prostheses from being rejected, making them coexist peacefully with surrounding tissues without impairing health? Moreover it is sometimes required that a prosthesis that has fulfilled its purpose should vanish.

This was the brain-teaser that the chemists took on. And they did not do too badly with it, in many ways owing to research conducted under the guidance of Doctor of Chemical Sciences Prof T. E. Lipatova in the Division of Polymerization Reaction Kinetics and Mechanism of the Institute of Chemistry of High Molecular Compounds, Ukrainian SSR Academy of Sciences, and later on in the same division after it was transferred to the Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences. Not only chemists but also biochemists, histologists, immunologists and surgeons participated in the scientific search.

The theoretical grounds for creating biologically compatible polymers were developed for the first time in the world. The principles of their "medical purity" were formulated. A tissue culture method was proposed for quick quantitative assessment of biocompatibility, and adopted by the USSR Ministry of Health as a mandatory test. The methods and procedures of synthesizing new polymers are original.

Such materials can be used in different areas of medicine. Following a comprehensive check-out on animals, they underwent clinical tests successfully. The chemists worked especially productively with children's surgeons and pancreas and liver specialists. Many successful operations were conducted by Doctor of Medical Sciences Prof N. B. Sitkovskiy, director of the Department of Children's Surgery, Kiev Medical Institute, and his colleagues.

"Porethane" protectors--soft, transparent, elastic and fearing no solvents--began to be used in the fight against serious illnesses such as aneurisms in major blood vessels. Children's surgeons in Kiev have already completed about 100 reconstructive operations of this sort. The new procedure has also been introduced at clinics in Moscow and Leningrad and in some Ukrainian oblast centers.

KL-3 medical adhesive is of special interest. It can substitute for traditional sutures during surgery. Development of an original gluing principle played an important role. For the first time in world practice a compound which glues living tissues securely and reliably was created. And this is not the only merit of the adhesive.

The adhesive has proven itself well not only in operations on blood vessels but also as a means for plugging the pancreatic duct in the case of a number of serious, frequently mortally dangerous illnesses including tumors, and in the case of organ transplants. More than 70 such operations were performed by Doctor of Medical Sciences Prof S. A. Shalimov, division director of the Kiev Scientific Research Institute of Clinical and Experimental Surgery.

Production of KL-3 adhesive and "porethane" protectors was organized with the permission of the USSR Ministry of Health at an experimental production operation of the Institute of Chemistry of High Molecular Compounds, Ukrainian SSR Academy of Sciences. The entire production procedure is based on using domestic raw materials.

As we can see, cooperation among chemical scientists, biochemists and specialists in clinical and theoretical medicine turned out to be productive. The fight against severe illnesses is now being waged more successfully. We believe that the author collective which was responsible for theoretical development of the new biodegradable medical polymers, for their experimental testing, for creation of the production procedures and for their introduction into practice deserve the Ukrainian SSR State Prize.

11004

CSO: 1841/62



## OZONE EFFECTS ON SATURATED POLYMERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 24, No 10, Oct 82  
(manuscript received 24 Jul 81) pp 2019-2035

RAZUMOVSKIY, S. D. and ZAIKOV, G. Ye., Institute of Chemical Physics, USSR  
Academy of Sciences

[Abstract] Effects of ozone on polymers include injurious and beneficial changes. The authors review the literature concerning protection of polymer materials from harmful ozone damage, and control of these processes for desired alterations of such materials. Wear increases along with creep in polystyrene, polyethylene and polypropylene articles. Adhesion to metals and dyes decreases and dielectric properties are reduced. Ozone processing has, however, been used on numerous polymers to enhance grafting of vinyl. Polymers with phenyl cycles are most resistant to ozone, while those with polycyclic structures or heteroatoms react more readily. Infrared spectra were analyzed to determine precise changes under ozone exposure. Changes in molecular mass were recorded for numerous polymers. Flexibility and the durability of seams varied according to the polymer type being assayed. Experimentally it was determined that surface reactions were more rapid by several orders than volume reactions. Ozone reacted with polycrystalline polyethylene and brought increased specific gravity. Compared to plasma or corona charge surface treatments, ozone brought steady accumulation of carbonyl and carboxyl groups. For polystyrene and polyethylene the kinetics of oxide compound formation were in agreement with a hypothesis on the predominant decomposition of primary peroxide radicals. Useful processes involving ozone to alter molecular mass of cellulose and other compounds are summarized. Figures 17; references 65: 31 Russian, 34 Western.  
[36-12131]

MECHANICAL BEHAVIOR OF POLYVINYLCHLORIDE AND ITS MIXTURE WITH RUBBER MODIFIER  
IN BROAD RANGE OF DEFORMATION RATES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 24, No 10, Oct 82  
(manuscript received 17 Jun 81) pp 2156-2159

YARYSHEVA, L. M., PAZUKHINA, L. Yu., STOCHES, R. N., ZAVAROVA, T. B.,  
BAKEYEV, N. F. and KOZLOV, P. V., Moscow State University imeni M. V. Lomonosov

[Abstract] The authors studied the importance of heat emission in determining properties of the title compounds. The modifier used was methylmethacrylate-butadiene-styrene, and tests were made through a wide range of rates to assay the effects of heat emission on deformation. Deviations from linearity are discussed for this process and an analogous one where water was the heat-dispersing agent. It was hypothesized that at low rates of stretching, deformation in air took place under close to isothermal conditions, but as the rate of stretching exceeded ca.  $1.58 \cdot 10^{-5}$  m/s, the conditions changed from isothermal to adiabatic and the effective temperature for formation of a weakening "neck" increased. Theoretical temperature values were also confirmed by direct measurements on the surface of the rubber film under deformation. The intensive heat emission at high deformation rates and the hampered heat removal led to a self-oscillation mechanism. The additive brought lesser temperature increases, and heat damage occurred at higher deformation rates. Figures 3; references 8: 5 Russian, 3 Western.  
[36-12131]

FIFTIETH ANNIVERSARY OF DEPARTMENT OF CHEMICAL TECHNOLOGY OF PLASTICS,  
MOSCOW CHEMICAL TECHNOLOGICAL INSTITUTE IMENI D. I. MENDELEYEV

Moscow PLASTICHESKIYE MASSY in Russian No 10, Oct 82 pp 3-6

KORSHAK, V. V. academician

[Abstract] The author reviews the history of the department, which he now heads, since its organization in 1932. Early research under the direction of Professor I. P. Losev concentrated on artificial and synthetic resins of modified phenolformaldehyde and ureaformaldehyde. Oxidation of paraffins and paraffin-containing petroleum products for detergents and other work with fatty acids also occupied the department's attention before its evacuation during World War II. Following the war, high-molecular compounds, heteroorganic high-molecular compounds and thermally durable polymers gained attention first in separate institutions, then as part of the title department. Areas of development for thermal-resistant polymers include stabilizers and new means of synthesis. Professor D. F. Kutepov has directed research on synthesis of triazine polymers and unsaturated polyesters with amino- and amido-nitrogen

atoms or metals of varying valency; research on synthesis of heteroorganic polymers has been directed by Associate Professor S. N. Zhivukhin. Various new polyphosphazenes have been synthesized and analyzed, and the nature and relationship of macromolecular bonds and their thermal, physicochemical and chemical properties studied. Study of thermal and chemical structuring has led to development of polyamidoimides that are as heat resistant as polyimides and better in technical properties. Other areas of research include ion-exchange materials, synthesis of adsorbents including boron- and carboran-containing sorbents, food and beverage stabilizers, water-soluble poly-electrolytes, vinyl-pyridine salts for purifying oil-contaminated sewage, Silar-type block-copolymers for various uses, hydrophobic and hydrophilic copolymers, and other products.  
[35-12131]

UDC 678.5.001(575.3)

#### CHEMICAL POLYMER RESEARCH IN THE TAJIK SSR

Moscow PLASTICHESKIYE MASSY in Russian No 10, Oct 82 pp 7-9

OBIDOV, Kh. K., chief, Department of Practical Implementation of Scientific and Technological Achievements, TaSSR GOSPLAN, KALONTAROV, I. Ya., president, Problem Council for Polymers, Division of Physico-Mathematical, Chemical and Geological Sciences, TaSSR Academy of Sciences

[Abstract] Polymer research in the Tajik SSR is related to the chemical, textile, cotton and machinebuilding industries. Polymer structures have been studied by infrared spectroscopy at the Laboratory for Optics and Spectroscopy, Physical-Technical Institute imeni S. U. Umarov, TaSSR Academy of Sciences, while chemical research has been done largely at the Chemical Institute imeni V. I. Nikitin, TaSSR Academy of Sciences. The achievements of this research are summarized under the sub-head of synthesis and study of properties of vinyl- and isopropenylethynyl polymers and copolymers, including high heat-resistant and superior dyes of piperidine derivatives and their use as water-soluble sorbents, coagulant and antiheparin polymers, and cellulose and polycaproamide biocide active dyes for preparing sterile clothing and dressings. Other research includes study of photo- and thermooxidative destruction and stabilization of polymers, particularly fibrous cellulose polymers from cotton varieties of the region, structural dye polymers and sorbents based on them such as polyacrylonitrile--from polyvinyl alcohol treated with sodium sulfide--and utilization of such scientific advances in cotton production. References 53: 49 Russian, 4 Western.  
[35-12131]

## STUDY OF POLYMER SYNTHESIS AND DEVELOPMENT OF PLASTIC PRODUCTION IN THE GEORGIAN SSR

Moscow PLASTICHESKIYE MASSY in Russian No 10, Oct 82 pp 9-11

KHANANASHVILI, L. M., TSISKARISHVILI, P. D. and CHACHIBAYA, A. Ya., Tbilisi State University, Institute of Physical and Organic Chemistry imeni P. G. Melikishvili, GSSR Academy of Sciences

[Abstract] Research at Tbilisi State University's departments of Chemistry of High-Molecular Compounds and Organic Chemistry is summarized, including pure and applied research of heterochain polymers such as organosilicon monomers and oligomers with phenethyl-, dicyclopentenyl- and thienyl groups at the silicon atom for microelectronics and electrical insulating and water-proofing coatings. Complex heterochain polyesters based on polycyclic biphenols and unique resin linthobiolite-rhabdopissite plastics that withstand tropical conditions have been developed at the institute. Since the raw materials for these compounds is abundant, further research is under way for its use involving the authors' and other scientific institutes in Soviet Georgia. It has resulted in a flame-resistant fiberglass fabric that is being produced at experimental levels, and electrical-conductive low-temperature heating elements that have been patented in the United States, France and Canada. Oligoorganic titanosiloxanes with internal framing groups at the titanium are being synthesized for textile and leather water proofing. Stratified plastics and use of secondary polymer raw materials are also being investigated in the Georgian republic. Objectives for plastics production in the republic during the current five-year plan are stated.  
[35-12131]

## COMPOSITION POLYMER MATERIALS IN POWER ENGINEERING

Moscow PLASTICHESKIYE MASSY in Russian No 10, Oct 82 pp 12-13

CHOGOVADZE, G. I., TOPCHIASHVILI, M. I. and KHANANASHVILI, L. M., Georgian Scientific Research Institute for Energy and Hydrotechnical Installations, Tbilisi State University

[Abstract] Composition polymer materials surpass traditional concrete and metals in corrosion and pitting resistance and other properties. The authors used an ultrasound method to study breakdown of such materials, and determined that the highest resistance to pitting was found in high pressure polyethylene, which surpassed 1Cr18N9T steel in this regard. Good pitting resistance was also recorded for epoxy polymers with andesite fillers. Microscopic examination showed that andesite has a very durable bond with epoxy binders as a result of its surface development, adsorption capability and chemical reactions.

with active epoxy-groups. Failure of various polymers subjected to ultrasound is related to the theories of Academician V. A. Kargin on the behavior of supermolecular structures when affected by external pitting forces. Epoxy glues used recently to seal cracks in concrete and reinforced concrete structures were studied to develop new foam-epoxy versions with improved strength and lack of residue. Dielectric properties that could be preserved after thermal treatment were also developed. Polymer compositions for low-temperature heating elements and fiberglass fabrics are also described. References 15 (Russian, including references to English patents).  
[35-12131]

UDC 678.544:620.197

#### ANTICORROSION ETHER-CELLULOSE COMPOSITIONS AND COATINGS BASED ON THEM

Moscow PLASTICHESKIYE MASSY in Russian No 10, Oct 82 pp 26-28

ZHIL'TSOV, V. Ye., ZEMSKOVA, Ye. Z., BABAYEVA, I. P., UVAROVA, N. A., ZAVADSKAYA, V. P. and LAYKHTER, L. B.

[Abstract] Since 10% of the world's metal is lost to corrosion, the authors sought to develop coatings of the title compositions that would help prevent these losses. They used K-150 ethylcellulose with 46.2% ethoxy-groups and acetylcellulose with acetyl numbers of 53-54%, benzotriazole inhibitors and synthetic fatty acids. The components were heated in oil to 190-200° C, then used to coat glass and tested for durability and technical properties. Results showed that when the benzotriazole and fatty acids ingredients were increased to five parts by mass, durability increased and hardness reduced, while the melting temperature remained constant. Varying the content of dimethylphthalate determined the optimal amount to be 225 parts by mass. Physical and mechanical properties of stabilized acetylcellulose coatings were better than those of unstabilized variants, and the most effective stabilizers were aluminum and calcium stearates and magnesium carbonate. With benzotriazole and synthetic fatty acids, stable and effective coatings were best produced using the base magnesium carbonate. Figures 3; references 6 (Russian).  
[35-12131]

## SOLID-PHASE LOW-TEMPERATURE POLYMERIZATION IN CYCLOPENTADIENE-TITANIUM TETRACHLORIDE SYSTEM, INDUCED BY MECHANICAL BLOW

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 266, No 6, Oct 82  
(manuscript received 31 May 82) pp 1410-1414

KABANOV, V. A., corresponding member, USSR Academy of Sciences, SERGEYEV, V. G., LUKOVKIN, G. M. and BARANOVSKIY, V. Yu., Moscow State University imeni M. V. Lomonosov

[Abstract] Rapid polymerization processes are known to take place on solid layers with unbalanced mixtures at temperatures as much as hundreds of degrees below melting points of balanced monomer crystals. Recently, explosive reactions of post-photo- and post-radiational chemical chlorination and hydrobromination of hydrocarbons under such circumstances have been shown to occur after tension leading to mechanical destruction of frozen layers at 4.2-7 K. The authors sought to induce the title polymerization as had been achieved in decomposition of solid explosives. Results showed that polymerization occurred in the title system much more rapidly under a mechanical blow than in spontaneous reactions. In special tests, localization was used to produce glassy layers of  $TiCl_4$  monomer, and the kinetics of its polymerization were studied after a mechanical blow. Although further data is needed, the results permitted preliminary description of the formation of the polymer chain. With other conditions being equal, the shift from one structure to another was regarded to occur via changes in concentration of potential active centers. Figures 3; references 13 (Russian).  
[53-12131]

## MECHANISM OF INCREASING IMPACT RESISTANCE OF POLYMERS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 266, No 5, Oct 82  
(manuscript received 25 Jan 82) pp 1152-1156

LUKOVKIN, G. M., VOLYNSKIY, A. L. and BAKYEV, N. F., Moscow State University imeni M. V. Lomonosov

[Abstract] The basic method for increasing resistance of polymers to impact has been introduction of finely dispersed rubber fillers with good adhesion, but the manner in which this process functions has remained unclear. Data has indicated that the basic mechanism for polymer failure at high-speed deformation has been local thermal destruction or melting or a combination. The authors studied the influence of deformation rate during stretching on the magnitude of the temperature increase for polyethylterephthalate. Data calculations are presented to show the good agreement of calculations with the

experimental results of other research, thus confirming the conclusion that very high temperatures develop during high-speed deformation leading to failure. Results for blow-resistant PC, PMMA and ABS-plastics confirmed these conclusions. The basic mechanism for increasing blow resistance was determined to be creation of numerous zones of transition to an oriented state, leading to decreases in local rates of plastic deformation and heat emission, thus avoiding heat destruction. Figure 1; references 13: 7 Russian (two likely translations), 6 Western.  
[60-12131]

UDC 541.486

STUDY OF EPOXY RESIN HARDENERS AS PRODUCTS OF REACTION OF CAPROLACTAM WITH METAL CHLORIDES

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 48, No 10, Oct 82  
(manuscript received 14 Oct 81) pp 1094-1098

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Institute of Organic Chemistry, UkSSR Academy of Sciences; Dnepropetrovsk  
Chemical and Technological Institute

[Abstract] To realize the full potential of epoxy resins substances that promote hardening based on  $\epsilon$ -caprolactam and metal chloride, the authors sought to explain the structure of such accelerators and their hardening mechanism. Procedures and results of infrared spectral analysis are summarized. The accelerators were used to harden an epoxy diene resin in isothermal conditions at 120°C. Their activity was assayed on the basis of electrokinetic data. Differences in IR spectra between caprolactam and metal chlorides bear witness to the conformational restructuring of the former's molecules, leading to durable complexes with Fe and Zn salts and unstable compounds with Ni, Co and Cu salts. X-rays showed that new complex compounds formed, not simply a mixture of metal salts and caprolactam. The nature of the central atom did not affect the catalytic capacity of the accelerator, but their capacity to harden was related to the ability to mix with resins and form complexes with active reagent groups. Figures 2; references 5: 2 Russian, 3 Western.  
[52-12131]

## DETERMINING CONSTANT OF CHAIN TRANSMISSION TO POLYMER BY PRIMARY INITIATOR RADICALS

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 48, No 10, Oct 82  
(manuscript received 30 Nov 81) pp 1085-1087

BOYKO, V. P. and GRISHCHENKO, V. K., Institute of Chemistry of High Molecular Compounds, UkSSR Academy of Sciences

[Abstract] In obtaining oligomers with functional end groups the chain transmission reaction is of importance since it affects the properties of eventual polymers. Transfer to monofunctional molecules has not previously been considered since in the transfer such molecules convert into bifunctional ones. The authors find that monofunctional molecules can be considered if it is accepted that transfer to them by primary radicals occurs with the same frequency as to bifunctional molecules. This hypothesis is developed mathematically. References 4 (Russian).

[52-12131]

UDC 542.953:547.5-31+547.415+547.551.1

## REACTION OF ALICYCLIC DIEPOXIDES WITH AMINES

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 48, No 10, Oct 82  
(manuscript received 16 Feb 81) pp 1101-1104

PAKTER, M. K., NIKONOVA, L. P., KARPOV, O. N. and BATOG, A. Ye., Ukrainian Scientific Research Institute for Plastics

[Abstract] Epoxy polymers based on alicyclic diepoxides have unique features, but require anhydride hardeners and initiators of cation polymerization that have not as yet been studied thoroughly. The authors tested the hypothesis that the attachment of amines to these epoxides takes place through epoxyketone regrouping leading to a polymer with an inadequate grid structure. They studied industrial alicyclic diepoxides with aniline and ethylenediamine as hardeners. Infrared and PMR spectra showed that under the experimental conditions used a typical polycondensation occurs of the oxidized alicyclic diepoxides with the amines. PMR-spectra demonstrated the durability of the cycloacetal group in reactions with amines. The reaction of the oxirane ring with amines in a temperature range of 60-150°C was found to be the same for alicyclic diepoxide as for heterocyclic epoxides. Figures 4; references 17: 15 Russian (two apparent translations), 2 Western.

[52-12131]



EFFECT OF THERMORADIATION PROCESSING ON RADIATION RESISTANCE OF GLASS

Leningrad FIZIKA I KHIMIYA STELKA in Russian Vol 8, No 4, Jul-Aug 82  
(manuscript received 14 May 81) pp 462-464

IKRAMOV, G. I., ISAYEV, I. Kh., KONONOV, A. N., PETROVSKIY, G. T. and  
YUDIN, D. M., State Optical Institute imeni S. I. Vavilov, Leningrad

[Abstract] Treatment of glass with heat during gamma-radiation is known to affect certain properties, e.g., radiation stability and optical features. The authors subjected production laser glass and tellurite glass of  $83\text{TeO}_2 \cdot 17\text{K}_2\text{O}$  glass, prepared under both oxidation and reduction conditions, to heat of 300, 350 and 400°C in a gamma-radiation stream of 3000 R/sec. They compared the spectra of radiation paramagnetic centers of irradiated glass to those of untreated glass. Results showed that the intensity of these spectra were lower for irradiated glass treated at 300°C, higher for those treated at 350°C, and that the glass melted at 400°C. Optical spectra were also dependent on the treatment temperature and the irradiation. Thermoradiation treatment generally improved transparency, a fact of great importance for fiber-optic applications. Figures 3; references 3 (Russian).  
[61-12131]

## RUBBER AND ELASTOMERS

UDC 541.64:539.199

### MOLECULAR MOBILITY IN UNFILLED AND FILLED CROSS-LINKED ORGANOSILICON RUBBERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 24, No 10, Oct 82  
(manuscript received 5 Jun 81) pp 2115-2124

LEVIN, V. Yu., ZHDANOV, A. A., SLONIMSKIY, G. L., MARTIROSOV, V. A.,  
KVACHEV, Yu. P., GOLUBKOV, G. Ye. and GRITSENKO, O. T., Institute of Hetero-  
organic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences

[Abstract] Study of molecular mobility permits determination of temperature zones of relaxation-phase shifts of importance in utilization of organosilicon rubbers. The authors studied polydimethylsiloxane rubber and variants with 0.5% methylvinylsiloxane or 0.3% methylvinylsiloxane and 8% methylphenylsiloxane, vulcanized with cumyl peroxide, and filled systems with 10-35 parts by weight of Aerosil. Dielectric and dynamic mechanical methods were used. The significance of partial crystallization and emergence of an amorphous phase is discussed. With reduction in the amount of filler, moisture absorption declined. Treated (at 470 K), or freshly prepared rubbers, showed glassing, crystallization and fusion under the experimental conditions. Aerosil particles were surrounded by water molecules whose motion in the temperature range of 190-220 K is explained by changes in dielectric characteristics of filled organosilicon rubbers, with significant dielectric losses and corresponding changes in dielectric permeability. The relaxational maximum at 190-220 K is determined by a "thawing" of mobility. Figures 9; references 14:  
9 Russian, 5 Western.  
[36-12131]

UDC 678.046

### EFFECT OF VULCANIZED MATRIX AND ACTIVE FILLERS ON VOLUME REDISTRIBUTION OF INGREDIENTS IN RESINS

Moscow KAUCHUK I REZINA in Russian No 10, Oct 82 (manuscript received 21 Jul 81)  
pp 11-13

DONTSOV, A. A., TARASOVA, G. I., LAPSHOVA, A. A. and GOLYAK, L. I., Scientific  
Research Institute for Resin Production

[Abstract] Migration of polar ingredients in SKMS-10 based resins to deep layers and to the surface resulting from temperature, pressure and solvent

vapors was studied to determine its practical importance. Composition before and after the effects of environmental factors was assayed by layer analysis. In contrast to earlier studies of a mixture containing thiuram D and characterized by a loose grid structure, a more "normal" grid structure was obtained by introducing zinc oxide to the mixture. Results showed that at room temperatures, no redistribution of thiuram D or neozone D took place in 100 hours. Data from these tests and earlier related studies permit the hypothesis that migration of undissolved or slightly dissolved ingredients is caused by capillary pressure arising during adsorption and condensation of liquid on dispersion particles of the ingredient. Reducing viscosity or increasing temperature also leads to changes in the intensity with which the studied processes take place, resulting from viscous and elastic properties of the matrix. Migration is judged to be a general process that occurs at various stages of processing and use. Figures 3; references 3: 2 Russian, 1 Western. [56-12131]

UDC 678.762.3.002.237

#### MODIFICATION OF RESINS BASED ON SKI-3 USING OLIGODIENES WITH FUNCTIONAL END GROUPS

Moscow KAUCHUK I REZINA in Russian No 10, Oct 82 (manuscript received 31 Mar 82) pp 13-15

ZYUZIN, A. P., LANOVSKAYA, L. M., MANUYLOVA, G. L. and KOFMAN, L. S.,  
Scientific Research Institute for Tire Production

[Abstract] Ways to improve use properties of protective resins based on diene rubber by modifying systems have been successful in many tests at improving resistance to thermal aging and fatigue. The system ODDI+RU [ODDI = oligodienedüsocyanate; RU = a molecular complex containing hexamethylenetetramine and resorcin], also offers the possibility of resisting cracking of such resins through the reaction of bifunctional oligomers with coagents during vulcanization and formation of hetero-chain polymers with subsequent grafting. The authors studied the mechanism of this process and also measured the reaction capability of SKI-GD resin in comparison to RU. Results showed that no components of the RU complex reacted with the SKI-GD during heating at 150°C for 50 minutes. SKI-3, on the other hand, has additives such as stearinic acid that react with oligodienedihydrazide. Addition of 1 mass unit of RU reduced the thermodurability coefficient while thermal aging increased, relative stretching declined and fatigue properties also worsened. Modification of the protective resin by any of the tested oligodienes without RU was regarded to be the best procedure. References 10 (Russian). [56-12131]

## THERMOPHYSICAL CHARACTERISTICS OF SYSTEMS BASED ON SKF-26

Moscow KAUCHUK I REZINA in Russian No 10, Oct 82 (manuscript received 29 Oct 81) pp 15-17

ABELIOV, Ya. A., KIRILLOV, V. N. and DONSKOY, A. A.

[Abstract] The globular structure of organofluorine rubbers changes during vulcanization and processing. The authors studied such changes in a broad range of temperatures of linear expansion and heat conductivity in systems based on SKF-26 with varying dispersion filler content. The results of calculated determination of two-component materials, according to properties of the initial ingredients, point to a monotonic change in properties as the content of a particular ingredient is increased. An experimental anomaly was related to restructuring of the supermolecular structure of the vulcanizate when high-dispersion fillers were added. For example, introduction of 5-7% white soot changed the structure of SKF-26 vulcanizate in a manner analogous to heat aging at 200°C for 24 hours. Experimental data provided the basis for determining glass point temperature dependence on the filler amount. Figures 4; references 12 (Russian).

[56-12131]

## MASS TRANSFER PROCESS OF 4010 NA PRODUCT IN POLYISOPRENE-POLYCHLOROPRENE SYSTEM

Moscow KAUCHUK I REZINA in Russian No 10, Oct 82 (manuscript received 18 Dec 81) pp 18-20

GRACHEVA, N. I., POTAPOV, Ye. E., GLAGOLEV, V. A. and KORNEV, A. Ye., Moscow Institute of Precision Chemical Technology imeni M. V. Lomonosov

[Abstract] Numerous experimental data have recently indicated that in formation of adhesion compounds of such different systems as resin-cord, resin-metal and multi-layer polymers, mass transfer of low molecular components plays an essential role. Tests have indicated that one reason for loss of adhesion in resin-metal compounds may be reaction of components migrating from SKI-3 with active polychloroprene groups. The authors studied this phenomenon on the basis of well-known 4010 NA antioxidant in the title system. While this compound had no significant effect on vulcanization in polyisoprene, in diffusion in polychloroprene it can react with halogen-containing groups to reduce their reactivity. Experimental data showed that the antioxidant had no fundamental effect on direct vulcanization processes in SKI-3, so that physicomachanical properties formed during its mass transfer do not determine the durability of element bonding in resin-metal compositions as a whole, as is found with "DFG." After migration, 4010 NA reacts with chloropolymer groups, and therefore, cannot take part in formation of adhesion compounds. Figures 3; references 8: 5 Russian, 3 Western.

[56-12131]

## ROLLER METHOD OF DETERMINING RHEOLOGICAL PROPERTIES OF ELASTOMERS

Moscow KAUCHUK I REZINA in Russian No 10, Oct 82 (manuscript received 29 Oct 81) pp 27-28

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[Abstract] Since rheological measurement equipment is in short supply and rubber-resin mixtures move rapidly during processing, direct measurement on processing equipment has gained preference. Assay of rheological parameters of elastomers and thermoplastics by rolling machines is familiar (Collin, 1974). Roller equipment has had limitations since it can be used only for already processed materials, whose behavior has been described a priori by the Ostwald de Ville rheological degree law. The proposed method uses a prepared curve of elastomer flow on roller machinery. The inter-roller clearance is a model of a slot rheometer with movable walls. Calculations are presented to demonstrate the adequacy of the procedure, which is within  $\pm 15\%$  of capillary viscosimeter measurements. Figures 2; references 16: 12 Russian, 2 Russian translations from English; 2 Western.  
[56-12131]

## WATER TREATMENT

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### EFFECT OF CONCENTRATION OF SUSPENDED SUBSTANCES ON PROCESS OF FOAM FORMATION IN EFFLUENT FROM ANTIBIOTIC PRODUCTION

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[Abstract] Aeration and mixing affects foam formation in purifying sewage, and they depend on such factors as the structure of surface-active-substance molecules and their concentration, temperature and pH factor, and impurities such as hardening salts, phosphates and other minerals. For example, intermediate-size minerals increase foam stability, but fine particles such as zinc, copper and lead sulfides and others break down the foam. Suspended particles often include mycellia particles from production of various antibiotics. The present study was conducted on such sewage by regulating introduction of mycellia particles and perlite into controlled solutions. Results showed that the composition of suspended substances was more important than their quantity. Small concentrations of perlite (up to 0.5 g/l) produced stable foam, while higher concentration caused the foam to break down. Increased concentration of suspended substances reduced the effectiveness of purification. Mycellia wastes should be eliminated from plant sewage, and flotation is ineffective for cleaning highly polluted sewage. Figure 1; references 2 (Russian).  
[41-12131]

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